

Chapter 6

Biohydrogen

6.1 Introduction

Hydrogen is the element of greatest abundance in the universe; however, its production from renewable resources remains a major challenge. Biohydrogen produced from biorenewables is a promising alternative for a sustainable energy source. Biohydrogen is a renewable biofuel produced from biorenewable feedstocks by chemical, thermochemical, biological, biochemical, and biophotolytical methods. As a sustainable energy supply with minimal or zero use of hydrocarbons, hydrogen is a promising alternative to fossil fuel. It is a clean and environmentally friendly fuel, which produces water instead of greenhouse gases when combusted.

The topic of renewable resources, biohydrogen in particular, includes energy security, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sectors of all countries in the world. Biohydrogen is an environmentally friendly alternative automotive fuel that can be used in an internal combustion engine. Due to its environmental merits, the share of biohydrogen in the automotive fuel market will grow fast in the next decade. There are several reasons for biohydrogen to be considered as a relevant technology by both industrialized and developing countries.

The most known industrial methods for producing hydrogen include steam reformation of natural gas, coal gasification, and splitting water with electricity typically generated from carbonaceous fuels. These energy-intensive industrial processes release carbon dioxide and other greenhouse gases and pollutants as byproducts. In addition to thermochemical hydrogen production by gasification, hydrogen can be produced biologically. There are currently two proposed pathways to use organisms for hydrogen production. Direct production through “photobiohydrogen” utilizes microorganisms capable of using solar photons to separate oxygen from water. Some microorganisms produce hydrogen naturally, and biotechnologies based on these microbial systems could lead to the development of clean, renewable sources of hydrogen.

The biorenewable feedstocks can be converted to petroleum-substitute fuels. The majority of the bioengineering strategies for biochemically derived fuels involve options for the disposition of organic matter produced via photosynthate. The bulk of the presently exploited photosynthate is directed toward the production of wood, food, and feed. During processing and consumption, biomass materials are generated which can be used for energy production via combustion, pyrolysis or biochemical conversions to ethanol, hydrogen, methane, and isopropanol. A second option is to engineer the photosynthetic apparatus to provide hydrogen. The third strategy is the cultivation of crops as energy sources via the foregoing processes. Biomass has the potential to accelerate the realization of hydrogen as a major fuel of the future. However, obtaining hydrogen from biomass has major challenges. There are no completed technology demonstrations. The yield of hydrogen is low from biomass since the hydrogen content in biomass is low to begin with (approximately 6% versus 25% for methane) and the energy content is low due to the 40% oxygen content of biomass.

6.2 Definition

The term biohydrogen (from the Greek words *bio* meaning *life* + *hydro* meaning *water* + *genes* meaning *born of* or *forming*) refers to non-fossilized and biodegradable organic material originating from plants, animals and microorganisms derived from biological sources. Biohydrogen is defined as hydrogen produced biologically (mostly by bacteria) as a biofuel from waste organic materials. Fermentative biohydrogen production plants are proposed industrial plants for the production of hydrogen. They would typically involve processes such as thermophillic fermentation, dark fermentation and/or photofermentation and gas cleaning. Biohydrogen production can also involve an element of anaerobic digestion where the methane from biogas is converted through steam reforming into hydrogen.

Hydrogen produced by microalga and bacteria is biohydrogen (Benemann, 1998). There are currently no practical biohydrogen production processes. However, several concepts have promise for near to long-term process development (Benemann, 1998).

Biohydrogen can comprehensively be described as hydrogen, which is produced chemically, thermochemically, biologically, biochemically, and biophotolytically from all biomass materials.

6.3 History

Sir E. Ray Lankester (1847–1929) was a prominent biologist who did research on a wide variety of organisms, from protozoa to mammals (Gest and Blankenship, 2004). In 1939 Hans Gaffron (German researcher), while working at the University

of Chicago, obtained fermentative and photochemical hydrogen from algae (Gaffron, 1939). Gaffron and Rubin first reported that *Scenedesmus*, a green microalga, evolved molecular hydrogen under light conditions after being kept in anaerobic and dark conditions (Gaffron and Rubin, 1942).

Gest and co-workers studied the metabolism of photosynthetic bacteria: the photochemical production of molecular hydrogen by growing cultures of photosynthetic bacteria (Gest and Kamen, 1949a; Ormerod and Gest, 1962). Gest and Kamen discovered the light-dependent production of H_2 and N_2 fixation by *Rsp. rubrum*. Subsequent studies revealed that many anoxygenic phototrophs have N_2 fixation capacity (Gest and Kamen, 1949b; Kamen and Gest, 1949), and that *Rsp. rubrum* can use H_2 and CO_2 (as the sole carbon source) for photoautotrophic growth in a synthetic medium (Ormerod et al., 1961). Hydrogen gas is a product of the mixed acid fermentation of *Escherichia coli*, the butylene glycol fermentation of *Aerobacter*, and the butyric acid fermentations of *Clostridium* spp. (Aiba et al., 1973).

The production of biohydrogen using bacteria and microalga started some 35 years ago with a meeting on "Biological Energy Conservation." Benemann and co-workers studied the hydrogen evolution from water using *Clostridium kluyveri* hydrogenase in 1973. Spinach chloroplast preparations were mixed with *Clostridium kluyveri* hydrogenase and ferredoxin. These findings indicate that hydrogen evolution from water and sunlight by photosynthetic processes could be a method for solar energy conversion. In the summer of 2001, researchers manipulated the photosynthetic process of spinach plants to produce hydrogen. But these biological means of hydrogen production are known only as laboratory experiments. Intense research persists to better understand ways to improve these hydrogen production methods. Biological hydrogen production has been known for over a century and research directed at applying this process to a practical means of hydrogen fuel production has been carried out for over a quarter century. Dark fermentation of biomass or wastes presents an alternative route to biological hydrogen production that has been little studied (Hallenbeck and Benemann, 2002).

Researchers have investigated hydrogen production with anaerobic bacteria since the 1980s (Nandi and Sengupta, 1998). Biohydrogen seems particularly suitable for relatively small-scale, decentralized systems, integrated with agricultural and industrial activities or waste processing facilities for the future renewable energy demands (Kotay and Das, 2008).

Direct hydrogen conversion from sunlight may offer higher theoretical efficiencies (Akkerman et al., 2002) compared to the 0.2 to 2.6% photosynthetic efficiencies in energy crops today (Klas, 2004). However, the scientific and technical feasibility of the process requires more development, and the costs of a photobioreactor will also be a challenge. Indirect biohydrogen involves oxygen inhibition of the electron transfer step and hydrogenase production of hydrogen from carbohydrates (Masukawa et al., 2002).

Several reviews have examined the potential of biological hydrogen production (Madamwar et al., 2000; Melis and Happe, 2001; Levin et al., 2004; Nath and Das, 2004; Prince and Kheshgi, 2005). Although microorganisms produce hydrogen by different mechanisms, the step can be represented by the simple chemical reaction

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$. This reaction is known to be catalyzed by either nitrogenase or hydrogenase enzymes. Although alternative biological hydrogen production pathways exist, each with its own set of advantages and disadvantages, the following discussion on biohydrogen production will focus on challenges that must be overcome to improve one type of biological hydrogen production known as biophotolysis. Biophotolysis holds potential for the scale of hydrogen production necessary to meet future energy demand. One advantage of biophotolysis is that it is a more efficient conversion of solar energy to hydrogen. Theoretically, the maximal energetic efficiency for direct biophotolysis is about 40% (Prince and Kheshgi, 2005). Appropriate enzymes then perform an electrochemical process that unites two electrons from the oxygen-producing step with two H^+ ions to make hydrogen as the other product. Indirect hydrogen production through photosynthesis in microalgae uses a dark fermentation step where the carbohydrate produced by photosynthesis is converted to hydrogen gas.

Hydrogen-intensive research work has already been carried out on the advancement of these processes, such as the development of genetically modified microorganisms, metabolic engineering, improvement of the reactor designs, use of different solid matrices for the immobilization of whole cells, biochemical assisted bioreactor, development of two-stage processes, etc., for higher H_2 production rates. Pilot plant trials of the photofermentation processes require more attention. Use of cheaper raw materials and efficient biological hydrogen production processes will surely make them more competitive with the conventional H_2 generation processes in the near future (Das and Veziroglu, 2008).

6.4 Hydrogen from Biorenewables via Biological Processes

Biological generation of biohydrogen technologies provide a wide range of approaches to generate hydrogen, including direct biophotolysis, indirect biophotolysis, photofermentations, and dark fermentation by a combination of these processes. It is important to develop hydrogen generation methods that are renewable like biohydrogen. Biohydrogen production processes are found to be more environmentally friendly and less energy intensive as compared to thermochemical and electrochemical processes.

There are three types of microorganisms that generate hydrogen: cyanobacteria, anaerobic bacteria, and fermentative bacteria. The cyanobacteria directly decompose water to hydrogen and oxygen in the presence of light energy by photosynthesis. Photosynthetic bacteria use organic substrates like organic acids. Anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into hydrogen. Biohydrogen can be generated using bacteria such as *Clostridia* by controlling temperature, pH, reactor hydraulic retention time (HRT) and other factors of the treatment system.

Biological hydrogen can be generated from plants by biophotolysis of water using microalgae (green algae and cyanobacteria), fermentation of organic com-

pounds, and photodecomposition of organic compounds by photosynthetic bacteria. To produce hydrogen by fermentation of biomass, a continuous process using a non-sterile substrate with a readily available mixed microflora is desirable (Hussy et al., 2005). A successful biological conversion of biomass to hydrogen depends strongly on the processing of raw materials to produce feedstock, which can be fermented by the microorganisms.

Biochemical and biological processes have many advantages:

1. No unwanted and hazardous byproducts are formed.
2. They occur at ambient temperatures and pressures.
3. No special equipment is needed.
4. All are renewable energy sources.
5. They are ecofriendly processes.

Green chemistry offers cleaner processes for energy abatement. Some of these energy conversion processes are:

1. Photosynthesis
2. Glycolysis
3. Nitrogen fixation
4. Fermentation processes

Although some of the steps in photosynthesis are still not fully understood, the overall photosynthetic reaction has been known since the 1800s. Jan van Helmont began the research of the process in the mid-1600s when he carefully measured the mass of the soil used by a plant and the mass of the plant as it grew. After noticing that the soil mass changed very little, he hypothesized that the mass of the growing plant must come from the water, the only substance he added to the potted plant. Photosynthesis is the most important biochemical process in which plants, algae, and some bacteria harness the energy of sunlight to produce food. Organisms that produce energy through photosynthesis are called photoautotrophs. Photosynthesis is a process in which green plants utilize the energy of sunlight to manufacture carbohydrates from carbon dioxide and water in the presence of chlorophyll (Viswanathan, 2006).

The initial process in photosynthesis is the decomposition of water into oxygen and hydrogen and oxygen will be released. The simplified photosynthesis pathways are given in Fig. 6.1 and Eqs. 6.1 and 6.2. The hydrogen and the carbon and oxygen of carbon dioxide are then converted into formaldehyde (Fig. 6.1). Then, a series of increasingly complex compounds results finally in a stable organic compound, hexose (typically glucose) (Eq. 6.1). This phase of photosynthesis utilizes stored energy and therefore can proceed in the dark. Hexose is polymerized into hexosan (typically glucosan) or carbohydrates (Eq. 6.2).

Glucose formation:



Glucosan formation via polymerization:



In general, the results of this process are the reverse of those in respiration, in which carbohydrates are oxidized to release energy, with the production of carbon dioxide and water. The intermediary reactions before glucose is formed involve several enzymes, which react with the coenzyme ATP (adenosine triphosphate) to produce various molecules. The main product, glucose, is the fundamental building block of carbohydrates (e.g., sugars, starches, and cellulose). Cellulose is used to build the rigid cell walls that are the principal supporting structure of plants. Plants are photoautotrophs, which mean they are able to synthesize food directly from inorganic compounds using light energy, instead of eating other organisms or relying on material derived from them. The energy for photosynthesis ultimately comes from absorbed photons and involves a reducing agent, which is water in the case of plants, releasing oxygen as a waste product. The light energy is converted to chemical energy, in the form of ATP and NADPH, using the light-dependent reactions and is then available for carbon fixation (Viswanathan, 2006).

Energy and carbon are obtained by organisms either directly or indirectly via the photosynthetic conversion of solar energy. The majority of the bioengineering strategies for biochemically derived fuels involve options for the disposition of organic matter produced via photosynthate. During processing and consumption, waste organic materials are generated which can be used for energy production via combustion, pyrolysis or biochemical conversions to ethanol, hydrogen, methane, and isopropanol.

Nitrogen fixation is the process by which nitrogen is taken from its relatively inert molecular form in the atmosphere and converted into nitrogen compounds useful for other chemical processes. Hydrogen gas is also released during the biological nitrogen fixation process.

A promising method is the biological production of hydrogen by fermentation. Fermentative hydrogen production is the fermentative conversion of organic substrate to biohydrogen manifested by a diverse group of bacteria using multienzyme systems involving three steps similar to anaerobic conversion. Fermentative/hydrolytic microorganisms hydrolyze complex organic polymers to monomers, which further convert to a mixture of lower molecular weight organic acids and alcohols by obligatory H_2 -producing acidogenic bacteria. The production of biohydrogen occurs in the second and third step of anaerobic degradation. Thereby, methanogenic bacteria must be inhibited to avoid the consumption of H_2 to produce CH_4 . The fermentative production of biohydrogen is characterized by a lower technical complexity compared to photofermentation. At that light-independent hydrogen production

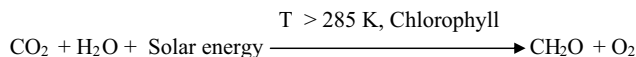


Fig. 6.1 Formaldehyde formation by the photosynthesis process

anaerobic microorganisms are always involved, converting the organic compounds to organic acids, hydrogen and carbon dioxide. The advantages of the fermentative hydrogen production are the broad spectrum of applicable substrates as well as high hydrogen production yields (Nandi and Sengupta, 1998; Hawkes et al., 2002).

Hydrogen production from the bacterial fermentation of sugars has been examined in a variety of reactor systems. Hexose concentration has a greater effect on H_2 yields than the hydraulic retention time (HRT). Flocculation also was an important factor in the performance of the reactor (Van Kinkel and Logan, 2005). Anaerobic fermentation was conducted to improve hydrogen fermentation of food waste in a leaching-bed reactor by heat-shocked anaerobic sludge, and also to investigate the effect of dilution rate on the production of hydrogen and metabolites in hydrogen fermentation (Han and Shin, 2004).

Direct photobiological hydrogen production by photosynthetic microorganisms is an active, developing field nowadays. Realization of technical processes for large-scale photobiological hydrogen production from water, using solar energy, would result in a major, novel source of sustainable, environmentally friendly and renewable energy. The unique biological process of photosynthesis in which solar energy is used to split water is combined with the natural capacity to combine obtained products into hydrogen, catalyzed by enzymes called hydrogenases. In nature, only cyanobacteria and green algae possess water oxidizing photosynthesis and hydrogen production, providing the option to form hydrogen from the Sun and water (Prince and Kheshgi, 2005; Viswanathan, 2006).

An increase in the production of hydrogen from biomass-derived glucose and attainment of the maximum molar yield of hydrogen, can be achieved through the enzymes of the pentose phosphate cycle in conjunction with a hyperthermophilic hydrogenase. This process includes centers on three $NADP^+$ ($NADP^+$ to form NADPH, nicotinamide adenine dinucleotide phosphate) dependent enzymes, glucose-6 phosphate dehydrogenase (G6PDH), 6-phosphogluconate dehydrogenase (6PGDH) and hydrogenase from *Pyrococcus furiosus*. The dehydrogenases are currently obtained from mesophilic sources (Viswanathan, 2006).

The enzymatic conversion of cellulosic waste to hydrogen via an in vitro enzymatic pathway involves the conversion of potential glucose sources such as cellulose by cellulases and plant sap (i.e., sucrose) by invertase and glucose isomerase to glucose. Glucose, the sugar produced by photosynthesis, is also renewable, unlike fossil fuels such as oil. The glucose substrate is then oxidized and the cofactor, $NADP^+$ is simultaneously reduced. The presence of a pyridine-dependent hydrogenase in this system causes the regeneration and recycling of $NAD(P)^+$ with the concomitant production of molecular hydrogen. The overall aim is to increase the production of hydrogen from biomass-derived glucose and achieve the maximum molar yield of hydrogen by employing the enzymes of the pentose phosphate pathway in conjunction with the hydrogenase from *Pyrococcus furiosus*. The main advantage over hydrogen production by fermentation is that close-to-theoretical yields of hydrogen from sugar would be possible (Das and Veziroglu, 2008; Viswanathan, 2006).

Hydrogen is produced in microorganisms by enzymes capable of reducing free protons to molecular hydrogen. Examples of these enzymes include hydrogenases and the nitrogenases. The production of hydrogen by these enzymes is usually cou-

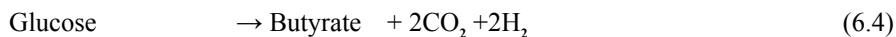
pled to some other biochemical processes. The energy used by these enzymes is usually in multiple steps from an organism's central energy input and is provided in the form of electron carriers such as ferredoxin or NADPH and energy yielding molecules like ATP. Obtaining useful amounts of hydrogen from microorganisms will require increasing the efficiency of hydrogenases and overcoming other obstacles. One problem is that some hydrogenases and nitrogenases are inhibited by oxygen. Oxygen is produced by photosystem II (PSII) during oxygenic photosynthesis. The driving force for reaction energy can be obtained by the breaking of bonds (the multistep breakdown of glucose to generate ATP and CO₂) or from electronic excitation. For example, plants, algae, cyanobacteria and photosynthetic bacteria can use light energy to raise electrons into higher energy states. In the case of plants, algae and cyanobacteria, the source of excitable electrons is water. The excited electrons are stripped from water, which then splits into oxygen and protons (Das and Veziroglu, 2008; Viswanathan, 2006).

6.4.1 *Hydrogen Production via Microbial Fermentation of Biomass*

In microbial fermentation of biomass, different waste materials can be used as substrates. A new and unique process has been developed when substrates such as carbohydrates are fermented by a consortium of bacteria; they produce hydrogen and carbon dioxide. Highly concentrated organic wastewater is one of the most abundantly available biomasses, which can be exploited for microbial conversion into hydrogen (Nath and Das, 2003). Municipal solid wastes and digested sewage sludge have the potential to produce large amounts of hydrogen by suppressing the production of methane by introducing low voltage electricity into the sewage sludge. The substrate from the acidogenesis of fruit and vegetable market wastes gives higher hydrogen evolution rates (about threefold) compared to synthetic medium. A mixed culture of photosynthetic anaerobic bacteria provides a method of utilization of a variety of resources for biohydrogen production (Miyaka et al., 1990).

6.4.2 *Anaerobic Hydrogen Production*

Anaerobic hydrogen production proceeds from photofermentation as well as without the presence of light. Anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into hydrogen.



The reactions involved in hydrogen production (Eqs. 6.3 and 6.4) are rapid and these processes do not require solar radiation, making them useful for treating large quantities of wastewater by using a large fermenter.

Since they cannot utilize light energy, the decomposition of organic substrates is incomplete. Further decomposition of the acetic acid is not possible under anaerobic conditions. Nevertheless, these reactions are still suitable for the initial steps of wastewater treatment and hydrogen production, followed by further waste treatment stages.

A new fermentation process that converts valueless organic waste streams into hydrogen-rich gas has been developed by Van Ginkel et al. (2001). The process employs mixed microbial cultures readily available in nature, such as compost, anaerobic digester sludge, soil, etc., to convert organic wastes into hydrogen-rich gas. The biodegradation efficiencies of the pollutants were examined by changing hydraulic retention time (HRT) as a main operating variable. An enriched culture of hydrogen-producing bacteria such as *Clostridia* was obtained by heat treatment, pH control and HRT control of the treatment system. The biohydrogen fermentation technology could enhance the economic viability of many processes utilizing hydrogen as a fuel source or as raw materials. Figure 6.2 shows the basic components of an anaerobic digestion system.

Anaerobic fermentative microorganisms, cyanobacteria and algae are suitable in biological production of hydrogen via hydrogenase due to reversible hydrogenases (Adams, 1990). Cyanobacteria and algae can carry out photoevolution of hydrogen catalyzed by hydrogenases. The reactions are similar to electrolysis involving splitting of water into oxygen and hydrogen (Gaffron, 1940).

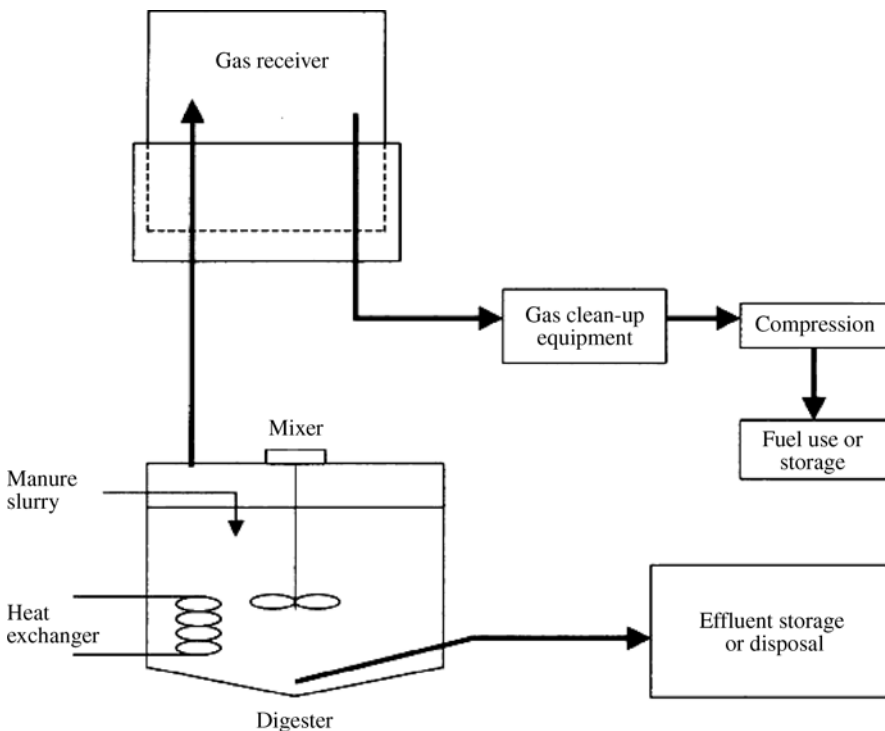


Fig. 6.2 Basic components of an anaerobic digestion system

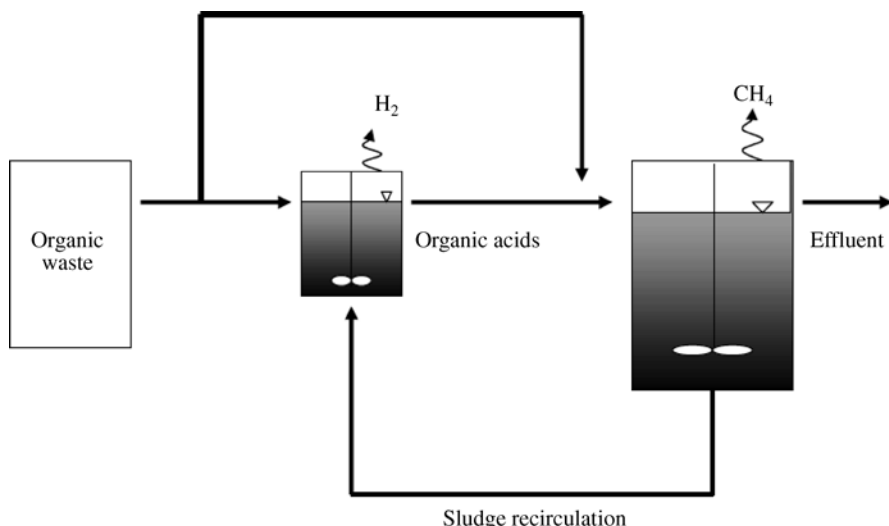


Fig. 6.3 Schematic diagram of the two-stage reactor system

Hydrogen-producing bacteria (*Clostridia*) were found to have growth rates about five to ten times higher than that of methane-producing bacteria (Van Ginkel et al., 2001; Sung, 2004). In a continuous flow bioreactor system, hydrogen production showed a declining trend at the later stage of reactor operation. Based on these findings, it is hypothesized that *Clostridia* may have gone through a phenomenon known as “degeneration” in which they lose their ability to produce hydrogen. Therefore, inoculating fresh mixed cultures may be a feasible way to maintain a sustainable hydrogen production. Based on this hypothesis, a two-stage anaerobic reactor has been proposed. The first-stage reactor is designed as a hydrogen-producing reactor whereas the second-stage reactor will be employed to cultivate fresh seed culture to perpetually supply the first one. Figure 6.3 shows the schematic diagram of the two-stage reactor system. The hydrogen-producing reactor has a total volume of 5 l with active volume of 3 l. The second stage has a total volume of 22 l, and the active volume is 18 l (Sung, 2004).

6.4.3 Biophotolytic Hydrogen Production

Biophotolysis is the action of light on biological systems that results in the dissociation of a substrate, usually water into molecular hydrogen and oxygen. Photosynthetic bacteria (e.g., *Rhodobactor*) can use broad organic substrates including lactic and acetic acids as the energy and carbon source under light irradiation. Photoautotrophic green microalgae and cyanobacteria use sunlight and carbon dioxide as the sole sources for energy and carbon.

Cyanobacteria are potential microbial species for hydrogen production via direct biophotolysis. By using nitrogenase and/or bi-directional hydrogenase, both heterocystous nitrogen-fixing strains and unicellular non-nitrogen-fixing strains are able to evolve hydrogen under special conditions. Hydrogen production increased significantly when replacing the air with argon (Howarth and Codd, 1985; Lindblad et al., 2002).

Under special conditions, the reducing equivalents (ferredoxin) can also be used by hydrogenase or nitrogenase to reduce protons for evolution of molecular hydrogen. Using Fe-hydrogenase and reduced ferredoxin is the substrate for hydrogen evolution. Anaerobic adaptation is needed for the cells to induce reversible Fe-hydrogenase. In order to overcome the inhibitive effect of oxygen on hydrogenase, various methods have been investigated with limited success, such as spatial separation of oxygen from hydrogen, immobilization of chloroplasts, electron carrier and hydrogenase, oxygen scavenging, and gas purging (Miura, 1995; Miura et al., 1997).

A major cost factor in large-scale hydrogen production is the photobioreactor that is usually characterized by surface area for light irradiation (Benemann, 1997). A hydrogen productivity based on reactor surface area can be found from the volumetric productivity and a critical optical length. Photobiological production of hydrogen from water (biophotolysis) requires efficient biological converters, microalgae, and low-cost photobioreactors. Microalgal strains must be developed that exhibit high hydrogen production rates and photosynthetic efficiencies in dense cultures at full solar intensities. The photobioreactor must expose the hydrogen-producing cultures to sunlight, while allowing recovery of the gas. A preliminary analysis is presented of a two-stage process in which microalgae are cultivated in large open ponds to produce a high carbohydrate biomass that then produces hydrogen in tubular photobioreactors. Photobioreactors constructed of inexpensive, commercially available glass tubes are proposed for such applications. Photobiological hydrogen production requires long-term research and development (Benemann, 1997).

Biological hydrogen production is often conducted in two stages under different atmospheric conditions, the first stage for cell growth followed by the second stage for hydrogen evolution. Nitrogen starvation is often applied at the end of the growth stage as an efficient metabolic stress to induce the activity of nitrogenase.

The atmosphere plays an important role in hydrogen evolution by cyanobacteria and could be a cost factor in large-scale hydrogen production. A nitrogen-free gas phase such as argon plus carbon dioxide gives a high hydrogen evolution rate (Weissman and Benemann, 1977).

Chlamydomonas reinhardtii, a facultative photoautotrophic and photoheterotrophic microalga, is the representative of green microalgae for biohydrogen research (Tsygankov, 2006; White and Melis, 2006). Other algal species such as *Chlorococcum littorale* and *Platymonas subcordiformis* are also investigated for hydrogen evolution (Guan et al., 2004). Gaffron and Robins first observed that unicellular microalga *Scenedesmus obliquus* could either use hydrogen as an electron donor in carbon dioxide fixation or evolve hydrogen under anaerobic conditions in dark or light environments (Gaffron and Robins, 1942). *Chlamydomonas reinhardtii* evolves large quantities of hydrogen gas when deprived of sulfur (Vijayaraghavan and Soom, 2006).

6.4.4 Dark Fermentative Hydrogen Production

Fermentative bacteria producing hydrogen may be cultivated in pure or mixed cultures selected from natural sources such as anaerobically digested sewage sludge or soil. The major pathways for microbial hydrogen production are driven by the anaerobic metabolism of pyruvate, formed during the catabolism of various substrates. Production of hydrogen by fermentation has been studied for a large group of pure fermentative bacteria, such as *Clostridia*. The biohydrogen production from bagasse based on dark fermentation was investigated using microorganisms like *Bacillus licheniformis*, *Clostridium pasteurianum* and *Enterobacter cloacae* (Vijayaraghavan and Soom, 2006).

Dark fermentation is the fermentative conversion of organic substrate to biohydrogen, it is a complex process manifested by a diverse group of bacteria by a series of biochemical reactions involving three steps similar to anaerobic conversion. Dark fermentation differs from photofermentation because it proceeds without the presence of light.

Dark fermentation for hydrogen production from wastes could be competitive with fossil fuel-derived hydrogen, providing a plausible approach to practical biohydrogen production. However, most of the research on biohydrogen production from organic wastes over the past two decades has focused on the use of photosynthetic bacteria (Sasikala et al., 1993). Benemann (1998) concluded that the dark fermentation of wastes is a promising process for biohydrogen production. The biohydrogen from carbohydrates was investigated using hyper thermophilic bacteria based on dark anaerobic fermentation (Claassen et al., 1999) and a high-rate anaerobic trickling filter (Groenestijn et al., 2002).

Scenedesmus, a green microalga, evolved molecular hydrogen under light conditions after being kept in anaerobic and dark conditions (Gaffron and Rubin, 1942). The responsible enzyme for hydrogen evolution is a reversible hydrogenase because it catalyzes the reaction in both directions (Mertens and Liese, 2004). Benemann and Weare (1974) reported that a nitrogen-fixing cyanobacterium, *Anabaena cylindrica*, evolved hydrogen and oxygen gas simultaneously in an argon atmosphere for several hours. The enzyme involved in hydrogen evolution is nitrogenase, which is responsible for the reduction of nitrogen into ammonia (Masukawa et al., 2002).

In photosynthesis, the reduced carbon is stored as endogenous carbohydrates, such as starch in microalgae and glycogen in cyanobacteria (Dauvillee et al., 2006). Following Gaffron and Rubin's discovery (Gaffron and Robins, 1942), studies on the mechanisms involved in hydrogen evolution have found that the electrons or reducing equivalents of hydrogenase and nitrogenase do not always come from water, but may sometimes originate from the intracellular energy reserve including carbohydrates (Miura et al., 1995; Antal and Lindblad, 2005). The algal fermentation conditions for the hydrogen production were investigated to improve the photobiological hydrogen production by a combination of a marine green alga *Chlamydomonas* sp. MGA161 and a marine photosynthetic bacterium *Rhodospseudomonas* sp. W-1S. The scaling-up of our biophotolysis system with algal-bacterial combination was carried out. The stably sustained starch accumulation and degradation

in the algal cells and hydrogen photoproduction from algal fermentation products by photosynthetic bacteria occurred in an alternating light-dark cycle (Miura et al., 1995).

The stored energy is released through fermentation of the endogenous carbohydrates in dark conditions, and the excess reducing power can be deposited by hydrogenase on protons forming molecular hydrogen (Gfeller and Gibbs, 1984). Hydrogen evolution from endogenous carbon reserve under dark anaerobic conditions looks very similar to the conventional anaerobic hydrogen fermentation, but the endogenous carbon reserve is made *in vivo* during photosynthesis. In this sense, the electrons or reducing equivalents in indirect biophotolysis are derived from water by photoautotrophic cells. This indirect biophotolysis, therefore, consists of two stages in series: photosynthesis for carbohydrate accumulation, and dark fermentation of the carbon reserve for hydrogen production. In this way, the oxygen and hydrogen evolutions are temporally and/or spatially separated (Benemann, 1996). Miura and co-workers proposed a process of hydrogen production via indirect biophotolysis by using natural light/dark cycles (Miura et al., 1997). According to this proposal, carbon dioxide is reduced to starch by photosynthesis in daytime, and the starch thus formed, is fermented to hydrogen gas and organic acids under anaerobic conditions during nighttime. The organic acids and other fermentative products can be further used for hydrogen evolution by photosynthetic bacteria under light irradiation (Melis and Melnicki, 2006).

Few studies have been conducted on fermentative hydrogen production by green microalgae. Compared with green microalgae, unicellular non-nitrogen-fixing cyanobacteria have attracted more research interest for hydrogen production via indirect biophotolysis. *Spirulina platensis* is a filamentous cyanobacterium cultivated at large commercial scales as a food supplement with high proteins, antioxidants and other nutrients. *S. platensis* NIES-46 accumulates high glycogen content (50% dry mass) in nitrogen-limited conditions and evolves molecular hydrogen at a moderate rate of 0.11 mmol/g dry wt/h after induction in dark and nitrogen atmosphere (Aoyama et al., 1987). For 1 mol of hydrogen evolved, the cells also release 1.4 mol of acetate, 0.65 mol of ethanol, 0.4 mol of formate and 0.1 mol of lactate as electron acceptors.

A unicellular non-nitrogen-fixing cyanobacterium *Gloeocapsa alpicola* CALU743 showed a high activity of reversible hydrogenase induced in dark anaerobic conditions (Serebryakova et al., 1998). In dark fermentation, 1 mol glucose and the strain produces 3.92 mol of hydrogen, 1.83 mol of CO₂, 1.97 mol of acetate, and small amounts of lactate and ethanol. The hydrogen yield is very close to the theoretical value when acetate is the sole fermentative product. The energy obtained in 4 mol of hydrogen is about 40% of the energy in 1 mol of glucose. The remainder of glucose energy is mainly left in 2 mol of acetic acid. The overall energy efficiency would therefore be significantly improved if acetate could be reused to form endogenous carbon reserve by facultative photoautotrophic cells in photosynthesis.

Carbohydrates are the preferred organic carbon source for hydrogen-producing fermentations. Glucose in the biomass yielded 2 and 4 mol H₂ per mol glucose with butyrate and acetic acid as their respective fermentation product. Hydrogen can be produced sustainably by anaerobic bacterial growth on carbohydrate-rich

substrates, giving organic fermentation end-products such as hydrogen and carbon dioxide.

Microbial community composition dynamics was studied during hydrogen fermentation from glucose in a fluidized-bed bioreactor (FBR) aimed at obtaining insight into the hydrogen fermentation microbiology and factors resulting in the instability of biofilm processes. FBR hydrogen production performance was characterized by an instable pattern of the prompt onset of hydrogen production followed by a rapid decrease. Gradual enrichment of organisms increased the diversity of the FBR attached and suspended growth phase bacterial communities during the operation. A high glucose loading rate favored the hydrogen production by an *Escherichia coli* affiliated strain. Decrease in H_2 production, associated with a shift from acetate–butyrate to acetate–propionate production, was due to changes in the FBR attached and suspended growth phase bacterial community compositions. During the shift, organisms, including potential propionate producers, were enriched in the communities while the proportion trend of *C. butyricum* decreased. Suggestions of reactions taking place during anaerobic, dark fermentation of glucose in the fluidized-bed bioreactor include (Koskinen et al., 2007):

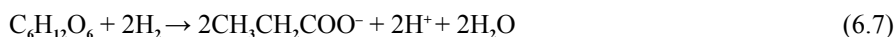
Ethanol formation:



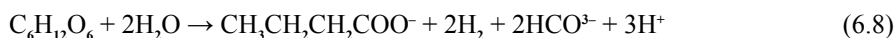
Acetate formation:



Propionate formation:



Butyrate formation:



6.5 Hydrogen from Biorenewables via Thermochemical Processes

Hydrogen can be produced from biorenewable feedstocks via thermochemical conversion processes such as pyrolysis, gasification, steam gasification, steam reforming of bio-oils, and supercritical water gasification (SWG) of biomass.

The strategy is based on producing hydrogen from biomass pyrolysis using a co-product strategy to reduce the cost of hydrogen. It has been suggested that only this strategy could compete with the cost of the commercial hydrocarbon-based technologies (Wang et al., 1998). This strategy will demonstrate how hydrogen and biofuel are economically feasible and can foster the development of rural areas when practiced on a larger scale. The process of biomass to activated carbon is an alternative route to hydrogen with a valuable co-product that is practiced commercially. The yield of hydrogen that can be produced from biomass is relatively low,

12–14% based on the biomass weight (Demirbas, 2005a). The proposed second process is fast pyrolysis of biomass to generate bio-oil and catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide.

In the pyrolysis and gasification processes, the water–gas shift is used to convert the reformed gas into hydrogen, and pressure swing adsorption is used to purify the product. The cost of hydrogen production from supercritical water gasification of wet biomass was several times higher than the current price of hydrogen from steam methane reforming (Demirbas, 2005a). The pyrolysis was carried out at moderate temperatures and steam gasification at the highest temperatures. The pyrolysis-based technology, in particular, because it has co-product opportunities, has the most favorable economics.

The yield from steam gasification increases with increasing water-to-sample ratio. The yields of hydrogen from the pyrolysis and the steam gasification increase with increase of temperature. In general, the gasification temperature is higher than that of pyrolysis and the yield of hydrogen from the gasification is higher than that of the pyrolysis. The highest yields (% dry and ash-free basis) were obtained from the pyrolysis (46%) and steam gasification (55%) of wheat straw, while the lowest yields from olive waste. The yield of hydrogen from supercritical water extraction was considerably high (49% by volume) at lower temperatures.

The catalytic aqueous phase reforming might prove useful for the generation of hydrogen-rich gas from carbohydrates extracted from renewable biomass and biomass waste streams. The biomass-derived hydrocarbons are suitable to hydrogen generation from biomass, as well as for the reforming.

It is believed that in the future biomass can become an important sustainable source of hydrogen. Biomass has the advantage of low environmental impact compared with that for fossil fuels. The price of hydrogen obtained by direct gasification of lignocellulosic biomass, however, is about three times higher than that for hydrogen produced by steam reforming of natural gas (Spath et al., 2000).

Hydrogen from organic wastes has generally been based on the following thermochemical reactions:

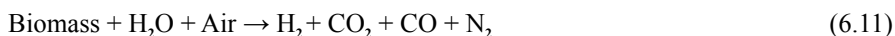
1. Production of hydrogen by pyrolysis of biomass



2. Production of hydrogen by catalytic steam gasification of biomass



3. Production of hydrogen by air gasification of biomass



Steam reforming is the major process for the production of hydrogen presently. This process has several disadvantages. For example, it is a thermally inefficient process (about 90% including the convection zone) and there are mechanical and maintenance issues. The process is difficult to control and reforming plants require a large capital investment. Hence to meet the increasing demand for this future fuel, alternatives to reforming processes are essential.

Biomass-derived synthesis gas can provide a renewable route to hydrogen. A novel bacterial process has been proposed as an alternative to the conventional high-temperature catalytic process for the production of hydrogen from synthesis gas via the water–gas shift (WGS) reaction. Hydrogen can be produced via pyrolysis or gasification of biomass resources such as agricultural residues like peanut shells, consumer wastes including plastics and waste grease, or biomass specifically grown for energy uses. Biomass pyrolysis produces a liquid product (bio-oil) that contains a wide spectrum of components that can be separated into valuable chemicals and fuels, including hydrogen.

6.5.1 Potential of Renewable Hydrogen Production

Hydrogen is produced today dominantly from carbonaceous raw materials. Milne et al. (2002) reported approximately 95% of the hydrogen produced comes from fossil fuels conversion, such as natural gas reforming. With the growing concern about global climate changes, the currently used way of producing hydrogen will have to change, as CO₂ carbon emission is always associated with such processes. Therefore alternative methodologies should be identified to overcome the shortage of this process. Using biomass as a hydrogen carrier in the near and mid-term appears viable in terms of technology, economy and environment as well as availability of sources. Even if without the subsequent sequestration of carbon, the whole process is still environment friendly as biomass is a CO₂-neutral resource in the life cycle (Chen et al., 2003).

Biomass has been considered as potential feedstock for gasification to produce syngas (H₂ + CO). An alternative approach to the production of H₂ from biomass begins with fast pyrolysis of biomass (Wang et al., 1997). Production of hydrogen gas by gasification of carbon with superheated steam was reported (Lower, 1963). The different methods of hydrogen production are: production from solid biomass (e.g., pellets of dedicated energy crops, waste biomass), fermentation of liquid manure and biological hydrogen production. The advantage of direct hydrogen production from biomass is that renewable energy sources can be utilized without the need of electrolysis thus leading to higher system efficiency and a more favorable overall result. Hydrogen can be extracted from hydrogen-rich biomass sources like wood chips and agricultural waste.

Biomass is available and obtainable in the world through the rational collection of byproducts from agricultural and forestry industries. The potential supply of biomass is significantly large as an energy crop.

Biomass can be used to produce hydrogen or hydrogen-rich gas via different technical pathways, i.e., anaerobic digestion, fermentation, metabolic processing, high-pressure supercritical conversion, gasification and pyrolysis. Compared with other pathways, gasification and pyrolysis appear technoeconomically viable at the current stage. A certain number of efforts have already been made to test gasification or pyrolysis of biomass for the production of hydrogen (Milne et al., 2002).

Those efforts can be categorized based on the types of biomass used, types of reactors (gasifiers or pyrolyzer), the addition of catalysts, end-products (e.g., hydrogen itself, hydrogen intermediates, hydrogen-rich gases) and gasifying medium used. The biomass types tested by previous researchers are residue coming from extraction of grass and lucern for protein, agricultural wastes (rice straw, wheat stalk), wood particles, municipal solid waste, almond shells, sawdust, black liquor, lignin, hazelnut shells, cotton and tobacco wastes, and plastic/rubber wastes (Demirbas et al., 1996; Caglar and Demirbas, 2002; Chen et al., 2003). The use of different catalysts such as dolomite, zeolites, potassium minerals, nickel-based compounds, platinum-based compounds, and metal oxides have been summarized in literature (Milne et al., 2002; Chen et al., 2002). As for the gasifying medium, the tested medium is steam, air, and oxygen. In addition, the gasification or pyrolysis process needs heating sources, and the used sources are electrical energy, combustion heat of fossil fuel or biomass char, solar energy, thermonuclear, and hydrothermal energy. Indirect pyrolysis of biomass to hydrogen through intermediates (pyrolysis oils) was also interestingly investigated (Chornet, 2001; Czernik et al., 2001).

6.5.2 Production of Hydrogen from Biomass via Pyrolysis

Pyrolysis dates back to at least ancient Egyptian times, when tar for caulking boats and certain embalming agents were made by pyrolysis. In the 1980s, researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced also condensed rapidly (Mohan et al., 2006).

Pyrolysis is the thermal decomposition of organic matter occurring in the absence of oxygen or when significantly less oxygen is present than required for complete combustion. Pyrolysis is the basic thermochemical process for converting biomass to a more useful fuel. Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon-rich gas mixture, an oil-like liquid and a carbon-rich solid residue. The products of pyrolysis can be gaseous, liquid, and/or solid. Flash pyrolysis describes the rapid, moderate temperature (675–875 K) pyrolysis that produces liquids. Biomass is heated at rates of 100–10 000 K/s and the vapor residence time is normally less than 2 s. The oil products are maximized at the expense of char and gas.

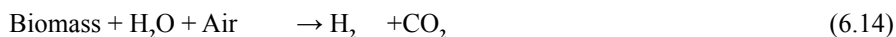
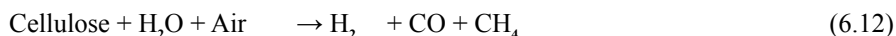
Pyrolysis is a process similar to gasification except generally optimized for the production of fuel liquids (pyrolysis oils) that can be used straight or refined for higher quality uses such as engine fuels, chemicals, adhesives, and other products. Pyrolysis typically occurs at temperatures in the range of 675 to 975 K. Pyrolysis and combustion of pyrolysis-derived fuel liquids and gases also produce the same categories of end-products as direct combustion of solids.

Fast pyrolysis utilizes biomass to produce a product that is used both as an energy source and a feedstock for chemical production. Considerable efforts have been made to convert wood biomass to liquid fuels and chemicals since the oil cri-

sis in the mid-1970s. Most work has been performed on wood, because of its consistency and comparability between tests. However, nearly 100 types of biomass have been tested, ranging from agricultural wastes such as straw, olive pits, and nut shells to energy crops such as miscanthus and sorghum. The following are affected by the pyrolysis reaction rate and the yield of the volatiles: the biomass composition and structure, heating rate, residence time, catalyst, and particle size. Although very fast and very slow pyrolyses of biomass produce markedly different products, the variety of heating rates, temperatures, residence times, and feedstock varieties found in the literature make generalizations difficult to define, in regards to trying to critically analyze the literature (Mohan et al., 2006).

Rapid heating and rapid quenching produced the intermediate pyrolysis liquid products, which condense before further reactions break down higher molecular weight species into gaseous products. High reaction rates minimize char formation. Under some conditions, no char is formed. At higher fast pyrolysis temperatures, the major product is gas. Many researchers have attempted to exploit the complex degradation mechanisms by conducting pyrolysis in unusual environments (Mohan et al., 2006). The main pyrolysis variants are listed in Table 6.1.

Pyrolysis is the simplest and almost certainly the oldest method of processing one fuel in order to produce a better one. Pyrolysis can also be carried out in the presence of a small quantity of oxygen (gasification), water (steam gasification) and hydrogen (hydrogenation). Hydrogen from organic materials has generally been based on the following pyrolysis reactions (Demirbas and Arin, 2004; Demirbas, 2008a):



If the purpose is to maximize the yield of liquid products resulting from biomass pyrolysis, a low-temperature, high heating rate, short gas residence time process would be required. For high char production, a low-temperature, low heating rate process would be chosen. If the purpose is to maximize the yield of fuel gas resulting from pyrolysis, a high-temperature, low heating rate, long gas residence time process would be preferred. It is believed that as the pyrolysis reaction progresses the carbon residue (semichar) becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases (Tran and Charanjit, 1978).

Five biomass samples (hazelnut shell, cotton cocoon shell, tea factory waste, olive husk and spruce wood) were pyrolyzed in a laboratory-scale apparatus designed for the purpose of pyrolysis (Demirbas, 2001, 2002a). Figure 6.4 shows the simple experimental setup of pyrolysis. The main element of the experimental device is a vertical cylindrical reactor of stainless steel, 127.0 mm in height, 17.0 mm inner diameter and 25.0 mm outer diameter inserted vertically into an electrically heated tubular furnace and provided with an electrical heating system power source, with a heating rate of about 5 K/s. The biomass samples ground

Table 6.1 Pyrolysis methods and their variants

Method	Residence time	Temperature, K	Heating rate	Products
Carbonation	Days	675	Very low	Charcoal
Conventional	5–30 min	875	Low	Oil, gas, char
Fast	0.5–5 s	925	Very high	Bio-oil
Flash-liquid ^a	< 1 s	< 925	High	Bio-oil
Flash-gas ^b	< 1 s	< 925	High	Chemicals, gas
Hydropyrolysis ^c	< 10 s	< 775	High	Bio-oil
Methanopyrolysis ^d	< 10 s	> 975	High	Chemicals
Ultrapyrolysis ^e	< 0.5 s	1275	Very high	Chemicals, gas
Vacuum pyrolysis	2–30 s	675	Medium	Bio-oil

^aFlash-liquid: Liquid obtained from flash pyrolysis accomplished in a time of < 1 s

^bFlash-gas: Gaseous material obtained from flash pyrolysis within a time of < 1 s

^cHydropyrolysis: Pyrolysis with water

^dMethanopyrolysis: Pyrolysis with methanol

^eUltrapyrolysis: Pyrolysis with very high degradation rate

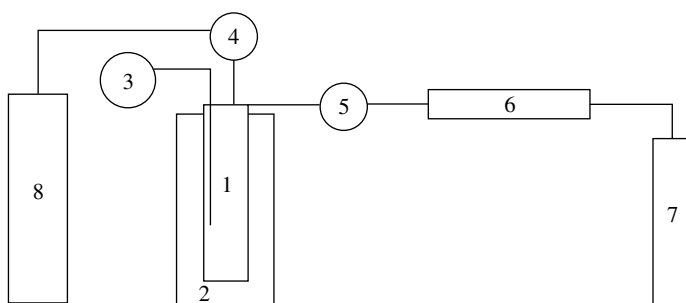


Fig. 6.4 Simple diagram of pyrolysis. 1 stainless steel tube, 2 electrical heater, 3 temperature control monitor, 4 nitrogen pressure control monitor, 5 product exit valve, 6 condenser, 7 oily products collecting vessel, 8 nitrogen tube

to 0–0.25 mm were filled in plastic sacks and nitrogen gas was blown over them to prevent possible oxidations. In each run, the sample (5 g of biomass) is introduced into the center of the tubular reactor.

The structural and elemental analyses (contents of C, H and O) of biomass samples are given in Table 6.2. Table 6.3 shows the yields of products from three biomass samples by pyrolysis at different temperatures. As seen in Table 6.3, the pyrolysis process yields gaseous products, tarry liquid, and tar. In general, the yields of gaseous products from each run increase with increasing pyrolysis temperature. The yields of gaseous products from the pyrolysis increase from 34.4 to 43.9% for hazelnut shell, from 35.1 to 47.4% for tea waste and from 32.1 to 40.7% for spruce wood with increasing of temperature from 700 to 950 K.

Table 6.2 Structural and elemental analyses of biomass samples (wt.% of dry, ash and nitrogen-free basis)

Sample	Hemicel- luloses	Cellu- lose	Lignin	Extrac- tives	C	H	O
Hazelnut shell	28.9	25.5	42.6	3.3	52.1	5.7	42.2
Tea waste	22.4	31.8	41.2	4.6	50.7	5.2	44.0
Olive husk	21.8	23.3	46.9	8.1	53.8	6.5	39.7
Cotton cocoon shell	12.0	34.7	49.7	3.6	53.0	6.2	40.8
Spruce wood	25.9	43.8	28.5	1.8	52.4	6.4	41.4

Table 6.3 Yields of products from biomass samples by pyrolysis at different temperatures (wt.% dry and ash-free)

Sample	Product	700 K	750 K	800 K	850 K	900 K	950 K
Hazelnut shell	Gas	34.4	36.1	38.0	39.4	41.3	43.9
	Liquid	32.9	31.7	30.4	29.6	28.4	26.9
	Char	32.7	32.2	31.6	31.0	30.3	29.2
Tea waste	Gas	35.1	37.8	40.3	42.9	45.3	47.4
	Liquid	35.5	34.4	33.3	32.1	30.4	29.0
	Char	29.4	27.8	26.4	25.0	24.3	23.6
Spruce wood	Gas	32.1	33.6	35.3	36.9	38.8	40.7
	Liquid	28.5	27.7	26.8	25.9	24.7	23.5
	Char	29.4	28.7	27.9	27.2	26.5	25.8

The compositions of gaseous products from three biomass samples by pyrolysis at different temperatures are given in Table 6.4. In general, the yields of hydrogen from pyrolysis tests of the biomass samples increase with increasing pyrolysis temperature. The total hydrogen-rich gaseous products increased with increasing pyrolysis temperature for the biomass sample (Demirbas, 2001). As can be seen in Table 6.4, the percentage of hydrogen in gaseous products from the samples of hazelnut shell, tea waste and spruce wood increased from 30.3 to 37.6%, 27.2 to 35.3% and 26.4 to 33.3% by volume, respectively, while the final pyrolysis temperature was increased from 700 to 950 K. The largest hydrogen yield (37.6%) was obtained from hazelnut shell at a temperature of 950 K (Table 6.4).

The pyrolysis yields of H_2 + paraffins obtained from biomass samples using different percentages of additives at different temperatures are presented in Table 6.5 (Caglar and Demirbas, 2002a, 2002b). The chemicals ($ZnCl_2$, Na_2CO_3 and K_2CO_3) were used as additives in the experiments. The yields of hydrogen + paraffins

Table 6.4 Compositions of gaseous products from biomass samples by pyrolysis at different temperatures (% by volume)

Sample	Gaseous product	700 K	750 K	800 K	850 K	900 K	950 K
Hazelnut shell	H ₂	30.3	31.2	31.8	32.8	34.4	37.6
	CO	22.6	24.7	26.4	27.1	27.4	28.3
	CO ₂	33.1	30.2	29.4	25.0	23.3	21.0
	CH ₄	6.5	6.0	6.3	6.5	7.1	6.1
	Olefins	1.0	1.1	0.8	0.8	0.7	0.9
Tea waste	H ₂	27.2	28.2	29.7	30.8	32.1	35.3
	CO	23.6	25.5	26.8	27.6	28.4	29.3
	CO ₂	34.0	31.2	29.8	25.5	24.3	22.0
	CH ₄	6.8	7.0	6.4	6.6	7.2	6.2
	Olefins	1.1	1.2	0.9	0.9	0.8	1.0
Spruce wood	H ₂	26.4	27.2	28.6	29.6	31.3	33.3
	CO	24.1	26.0	27.4	29.1	29.2	30.3
	CO ₂	34.5	31.7	30.3	26.9	25.1	23.0
	CH ₄	6.9	7.0	6.4	6.7	7.3	6.3
	Olefins	1.2	1.2	0.9	1.0	0.9	1.1

(mainly CH₄) from the biomass samples generally increased with increasing the pyrolysis temperature and percentage of additive. The highest (70.3% by volume) yield of hydrogen + paraffins was obtained from ZnCl₂ run with 13% additive of biomass sample.

Figures 6.5 to 6.7 show the effect of temperature on yields of H₂ + paraffins obtained from biomass samples by pyrolysis. As can be seen in Figs. 6.5 to 6.7, the percentage of H₂ + paraffins in gaseous products obtained from the samples of hazelnut shell, tea waste and spruce wood increased, while the final pyrolysis temperature was increased from 700 to 950 K.

Black liquor, a byproduct of the papermaking alkaline Kraft process (or sulfate method), is an important liquid fuel in the pulp and paper industry. Chemically, black liquor is a mixture of several basic elements where the largest fractions are carbon, oxygen, sodium and sulfur. The black liquor composition was assumed to be C₁₀H_{12.5}O₇Na_{2.4}S_{0.36} (Backman et al., 1993; Salmenoja, 1993). The black liquors can be converted to gaseous, liquid and char products by pyrolysis. Table 6.6 shows the average chemical composition of gaseous products from the precipitate from black liquor in the pyrolysis reactor at different temperatures (Demirbas and Caglar, 1998).

Table 6.5 Pyrolysis yields of H₂ + paraffins obtained from cotton cocoon shell and olive husk by using different percents of additives at different temperatures (% by volume)

Sample	Additive	Amount of additive (wt.% of sample)	Temperature (K)			
			775	925	975	1025
Cotton cocoon shell	None	—	30.4	32.0	36.3	44.4
Olive husk	None	—	48.2	54.1	52.4	54.5
Cotton cocoon shell	ZnCl ₂	7	46.4	48.1	50.0	44.9
Olive husk	ZnCl ₂	7	57.7	58.6	61.2	61.7
Cotton cocoon shell	Na ₂ CO ₃	7	33.3	33.8	41.5	44.5
Olive husk	Na ₂ CO ₃	7	47.0	55.3	58.2	57.0
Cotton cocoon shell	K ₂ CO ₃	7	40.8	43.4	45.7	45.6
Olive husk	K ₂ CO ₃	7	48.5	51.3	53.2	61.7
Cotton cocoon shell	ZnCl ₂	10	52.1	53.4	55.2	57.5
Olive husk	ZnCl ₂	10	57.3	61.1	61.9	69.4
Cotton cocoon shell	Na ₂ CO ₃	20	34.9	42.2	50.2	49.3
Olive husk	Na ₂ CO ₃	20	46.6	49.0	53.5	58.6
Cotton cocoon shell	K ₂ CO ₃	20	46.1	42.0	47.7	52.5
Olive husk	K ₂ CO ₃	20	49.6	53.3	58.8	59.9
Cotton cocoon shell	ZnCl ₂	13	56.1	59.3	58.4	59.9
Olive husk	ZnCl ₂	13	58.2	61.0	67.2	70.3
Cotton cocoon shell	Na ₂ CO ₃	33	41.2	44.5	47.8	50.7
Olive husk	Na ₂ CO ₃	33	48.0	51.9	60.8	62.9
Cotton cocoon shell	K ₂ CO ₃	33	43.0	47.2	52.6	51.9
Olive husk	K ₂ CO ₃	33	46.0	51.4	59.1	62.6
Cotton cocoon shell	Na ₂ CO ₃	47	50.9	45.6	45.7	45.6
Olive husk	Na ₂ CO ₃	47	48.2	49.3	50.5	48.2
Cotton cocoon shell	K ₂ CO ₃	47	48.2	45.1	45.0	47.3
Olive husk	K ₂ CO ₃	47	47.2	47.5	55.8	57.4

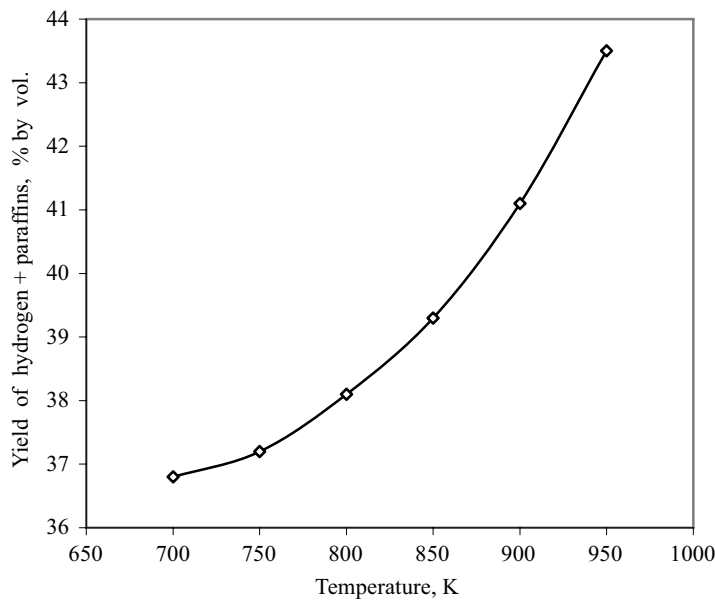


Fig. 6.5 Pyrolysis yields of H₂ + paraffins from hazelnut shells at different temperatures

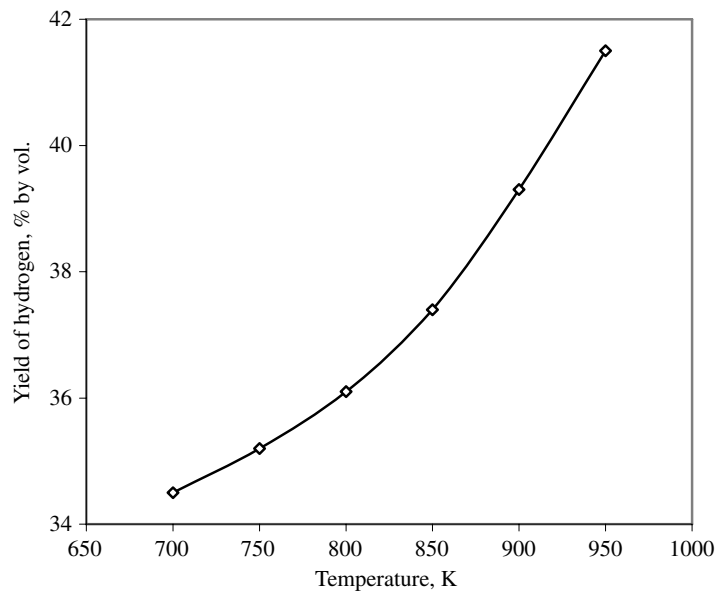


Fig. 6.6 Pyrolysis yields of H₂ + paraffins from tea waste at different temperatures

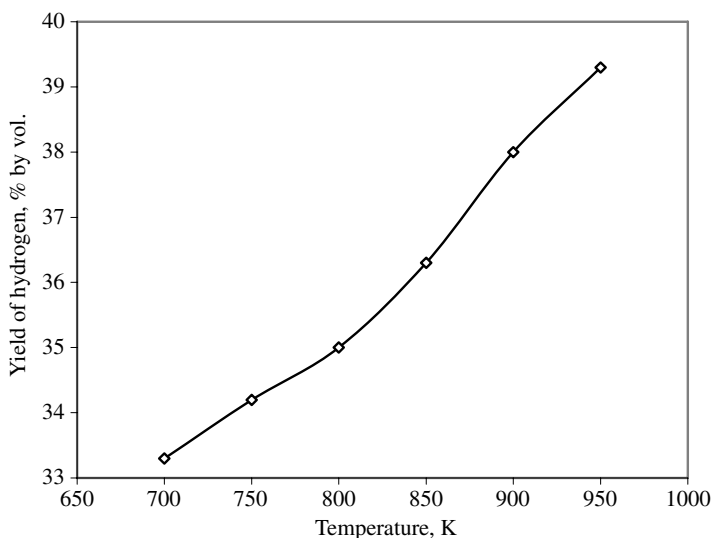


Fig. 6.7 Pyrolysis yields of H_2 + paraffins from spruce wood at different temperatures

Table 6.6 Average chemical composition of gaseous products from the precipitate from black liquor at different temperatures

Temperature (K)	Gas composition (% by volume)			
	H	CO	CO	CH ₄
295–675	11.3 ± 0.9	29.0 ± 0.8	26.5 ± 0.4	13.1 ± 0.7
295–825	14.1 ± 0.8	40.8 ± 0.5	19.9 ± 0.4	12.7 ± 0.6
295–825 ^a	31.7 ± 1.9	18.7 ± 0.7	30.1 ± 0.6	8.5 ± 0.3
295–925	18.4 ± 0.5	36.0 ± 0.4	15.9 ± 0.5	14.7 ± 1.1
295–925 ^a	36.4 ± 0.7	14.6 ± 0.3	32.3 ± 0.6	9.9 ± 0.4

^a3% K_2CO_3 of the samples used as catalyst

6.5.3 Production of Hydrogen from Biomass via Gasification

Biomass gasification has attracted the highest interest among the thermochemical conversion technologies as it offers higher efficiencies in relation to combustion, whereas flash pyrolysis is still in the development stage. When heated in a controlled atmosphere, biomass converts to synthesis gas, which primarily consists of carbon monoxide (CO), carbon dioxide (CO_2), and hydrogen (H_2). Gasification technology has been under intensive development over the last two decades. Large-scale demonstration facilities have been tested and commercial units are in operation worldwide.

Power generation from gaseous products from biomass gasification is found to be the most promising biomass gasification technology. Gasification technologies provide the opportunity to convert renewable biomass feedstocks into clean fuel gases or synthesis gases. The synthesis gas includes mainly hydrogen and carbon monoxide, which is also called syngas ($H_2 + CO$). Biosyngas is a gas rich in CO and H_2 obtained by gasification of biomass (Maschio et al., 1994; Demirbas, 2002b).

Gasification, one of thermochemical conversion routes, is widely recognized at present because its end-product gas can find flexible application by industries or by home users, particularly in decentralized energy production coupled with microturbine/gas, turbine/engine, boilers, even fuel cells (Chen et al., 2004). Gasification of biomass is a well-known technology that can be classified depending on the gasifying agent: air, steam, steam–oxygen, air–steam, O_2 -enriched air, etc.

Gasification describes the process in which oxygen-deficient thermal decomposition of organic matter primarily produces synthesis gas. Gasification is a combination of pyrolysis and combustion. Gasification typically refers to conversion of solid or liquid carbon-based materials by direct internal heating provided by partial oxidation using substoichiometric air or oxygen to produce fuel gases (synthesis gas, producer gas), principally CO, H_2 , methane, and lighter hydrocarbons in association with CO_2 and N_2 depending on the process used. Alternative configurations using either indirect heating methods such as externally fired burners or autothermal methods using exothermic reducing reactions have been demonstrated.

Gasification has more potential for near-term commercial application than other thermochemical processes. Benefits of gasification over combustion include more flexibility in terms of energy applications, more economical and thermodynamic efficiency at smaller scales, and potentially lower environmental impact when combined with gas cleaning and refining technologies. An efficient gasifier will decompose high molecular weight organic compounds released during pyrolysis into low molecular weight, non-condensable compounds in a process referred to as tar cracking. Undesirable char that is produced during gasification will participate in a series of endothermic reactions at temperatures above $800^\circ C$, which converts carbon into a gaseous fuel. Typically gaseous products include CO, H_2 , and CH_4 . Fischer–Tropsch processes may be used to upgrade gaseous products to liquid fuels through the use of catalysts (Sect. 3.8). Gasification requires feedstocks that contain less than 10% moisture.

Gasification is a form of pyrolysis, carried out in the presence of a small quantity of oxygen at high temperatures in order to optimize the gas production. The resulting gas, known as producer gas, is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen. The gas is more versatile than the original solid biomass (usually wood or charcoal): it can be burnt to produce process heat and steam, or used in gas turbines to produce electricity.

Biomass gasification technologies are expected to be an important part of the effort to meet these goals of expanding the use of biomass. Gasification technologies provide the opportunity to convert renewable biomass feedstocks into clean fuel gases or synthesis gases. Biomass gasification is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency, and to reduce the investment costs of biomass electricity generation through the use of

gas turbine technology. High efficiencies (up to about 50%) are achievable using combined-cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam for use in a steam turbine. Economic studies show that biomass suffocation plants can be as economical as conventional coal-fired plants.

Biomass gasification technologies have historically been based upon partial oxidation or partial combustion principles, resulting in the production of a hot, dirty, low heating value gas that must be directly ducted into boilers or dryers. In addition to limiting applications and often compounding environmental problems, these technologies are an inefficient source of usable energy.

The comparison of the environmental impact of biomass use in gasifiers and incinerators is very important when considering the effective use of biomass. However, high alkali content in biomass can form compounds with low melting temperature during combustion. The low melting ash constituents can induce in-bed agglomeration, in addition to fouling and corrosion problems.

The energy crisis of the 1970s brought a renewed interest to the topic of biomass. The technology was perceived as a relatively cheap indigenous alternative for small-scale industrial and utility power generation in those developing countries that suffered from high world market petroleum prices and had sufficient sustainable biomass resources. In the beginning of the 1980s at least 10 (mainly European) manufacturers were offering small-scale wood and charcoal-fired power plants (up to approximately 250 kW_e). At least four developing countries (Philippines, Brazil, Indonesia, India) started gasifier implementation programs based on locally developed technologies. Figure 6.8 shows the system for power production by means of biomass gasification. The gasification system of biomass in fixed-bed reactors provides the possibility of combined heat and power production in the power range of 100 kW_e up to 5 MW_e. A system for power production by means of fixed-bed gasification of biomass consists of the main unit gasifier, gas cleaning system and engine.

Commercial gasifiers are available in a range of sizes and types, and run on a variety of fuels, including wood, charcoal, coconut shells and rice husks. Power output is determined by the economic supply of biomass, which is limited to 80 MW in most regions. The producer gas is affected by various gasification processes from various biomass feedstocks. Table 6.7 shows composition of gaseous products from various biomass fuels by different gasification methods.

The relative simplicity of the gasification system enables its operation to be within the technical expertise of most operators who are experienced with conventional boilers and furnaces, and results in favorable project economics. Its modular design allows a wide range of scale-up or scale-down possibilities, so the systems can vary in size from about one ton per hour of residue to 20 tons per hour or larger, with the size being limited only by biomass availability.

The system can gasify a wide variety of biomass wastes and other organic materials generated by many industries. It has gasified, and in most cases has data on expected fuel composition, char analyses, and emissions analyses from the syngas produced for the following feedstocks: hardwood and pine saw dust, bark/hogged fuel, sander/grinder dust from panel board mills, pulp and paper mill sludge, whole

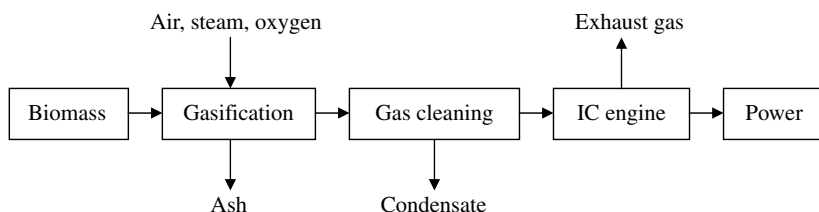


Fig. 6.8 System for power production by means of biomass gasification

Table 6.7 Composition of gaseous products from various biomass fuels by different gasification methods (% by volume)

H ₂	CO ₂	O ₂	CH ₄	CO	N ₂
10–19	10–15	0.4–1.5	1–7	15–30	43–60

and ground rice hulls, sugar cane bagasse, sewage sludge, the cellulosic fraction of municipal solid waste, and several grades of lignite and subbituminous coal.

The main steps in the gasification process are:

- Step 1. Biomass is delivered to a metering bin from which it is conveyed with recycled syngas or steam, without air or oxygen into the gasifier.
- Step 2. The material is reformed into a hot syngas that contains the inorganic (ash) fraction of the biomass and a small amount of unreformed carbon.
- Step 3. The sensible heat in the hot syngas is recovered to produce heat for the reforming process.
- Step 4. The cool syngas passes through a filter and the particulate in the syngas is removed as a dry, innocuous waste. The clean syngas is then available for combustion in engines, turbines, or standard natural gas burners with minor modifications.

Fixed-bed gasifiers are the most suitable for biomass gasification. Fixed-bed gasifiers are usually fed from the top of the reactor and can be designed in either updraft or downdraft configurations. The product gases from these two gasifier configurations vary significantly. At a larger scale, fixed-bed gasifiers can encounter problems with bridging of the biomass feedstock. This leads to uneven gas flow. Achieving uniform temperatures throughout the gasifier at large scales can also be difficult due to the absence of mixing in the reaction zone. Most fixed-bed gasifiers are air-blown and produce low-energy gases (Stevens, 2001).

With fixed-bed updraft gasifiers, the air or oxygen passes upward through a hot reactive zone near the bottom of the gasifier in a direction counter-current to the flow of solid material. Exothermic reactions between air/oxygen and the charcoal in the bed drive the gasification process. Heat in the raw gas is transferred to the bio-

mass feedstock as the hot gases pass upward, and biomass descending through the gasifier sequentially undergoes drying, pyrolysis, and finally gasification. Fixed-bed updraft gasifiers can be scaled up; however, they produce a product gas with very high tar concentrations. This tar should be removed for the major part from the gas, creating a gas-cleaning problem.

Figure 6.9 shows a schematic diagram of an updraft fixed-bed gasifier. In the drying zone, feedstock descends into the gasifier and moisture is removed using the heat generated in the zones below by evaporation. In the distillation zone, pyrolysis and partial oxidation takes place using the thermal energy released by the partial oxidation of the pyrolysis products. Tar yields can range from 0.1% (downdraft) to 20% (updraft) or greater in the product gases. The oxidation reactions of the volatiles are very rapid and the oxygen is consumed before it can diffuse to the surface of the char. In the reduction zone (often referred to as gasification zone) the char is converted into product gas by reaction with the hot gases from the upper zones. Depending on the end-use, it is necessary to cool and clean the gas in order to remove as much water vapor, dust and pyrolytic products as possible from the gas, especially if it is to be used in an internal combustion engine.

Figure 6.10 shows a schematic diagram of a downdraft fixed-bed gasifier. Fixed-bed downdraft gasifiers were widely used in World War II for operating vehicles and trucks. During operation, air is drawn downward through a fuel bed; the gas in this case contains relatively less tar compared with the other gasifier types. Fixed-bed downdraft gasifiers are limited in scale and require a well-defined fuel, making them not fuel-flexible.

Fluidized-bed (FB) gasifiers are a more recent development that takes advantage of the excellent mixing characteristics and high reaction rates of this method of gas-solid contacting. Examples of the FB gasifier systems are the bubbling fluidized-bed (BFB) gasifiers, the entrained-bed (EB) gasifiers, and the circulating fluidized-bed (CFB) gasifiers.

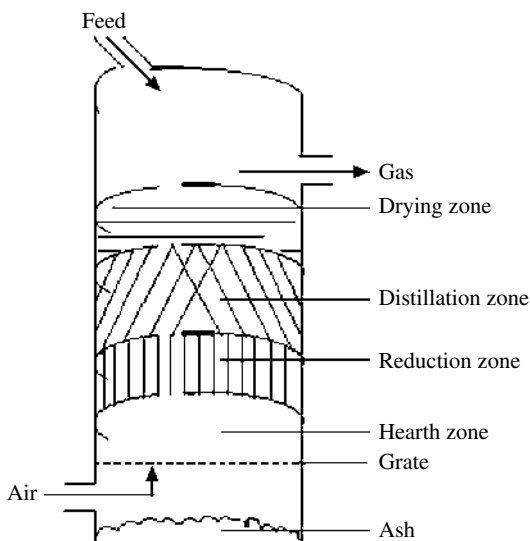
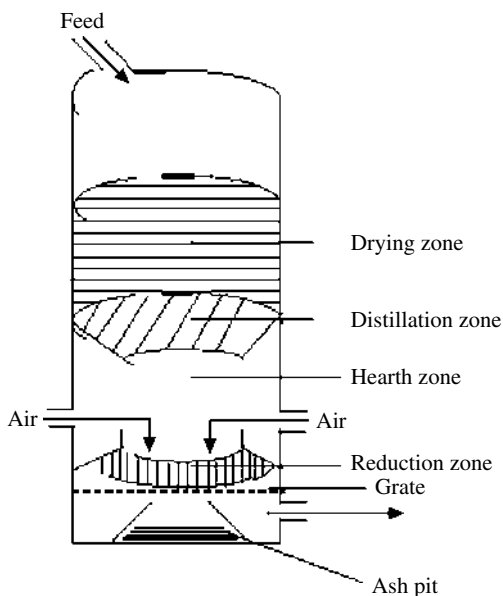


Fig. 6.9 Schematic diagram of an updraft fixed-bed gasifier

Fig. 6.10 Schematic diagram of a downdraft fixed-bed gasifier



The FB gasifiers are typically operated at 1050–1250 K (limited by the melting properties of the bed material) and are therefore not generally suitable for coal gasification, as due to the lower reactivity of coal compared to biomass, and higher required temperature (> 1550 K). Heat to drive the gasification reaction can be provided in a variety of ways in FB gasifiers. Direct heating occurs when air or oxygen in fluidizing gas partially oxidizes the biomass and heat is released by the exothermic reactions that occur. Indirect heating methods such as internal heat exchangers, using pre-heated bed material, or other means can also be used to drive the gasification reactions (Stevens, 2001). The BFB gasifier tends to produce a gas with tar content between that of the updraft and downdraft gasifiers. Some pyrolysis products are swept out of the fluid bed by gasification products, but are then further converted by thermal cracking in the freeboard region (Warnecke, 2000). The CFB gasifiers employ a system where the bed material circulates between the gasifier and a secondary vessel. The CFB gasifiers are suitable for fuel capacity higher than 10 MWth (Susta et al., 2003). The FB gasifier, and the CFB gasifier systems are given in Fig. 6.11.

6.5.3.1 Biomass Gasification Chemistry

Gasification of solid fuels to yield a mixture of H_2 and CO (syngas), followed by water–gas shift conversion to produce H_2 and CO_2 , are well-established processes (Patil, 1987). Gasification is a complex thermochemical process that consists of a number of elementary chemical reactions, beginning with the partial oxidation of a biomass fuel with a gasifying agent, usually air, oxygen, or steam. The chemical reactions involved in gasification include many reactants and many possible reac-

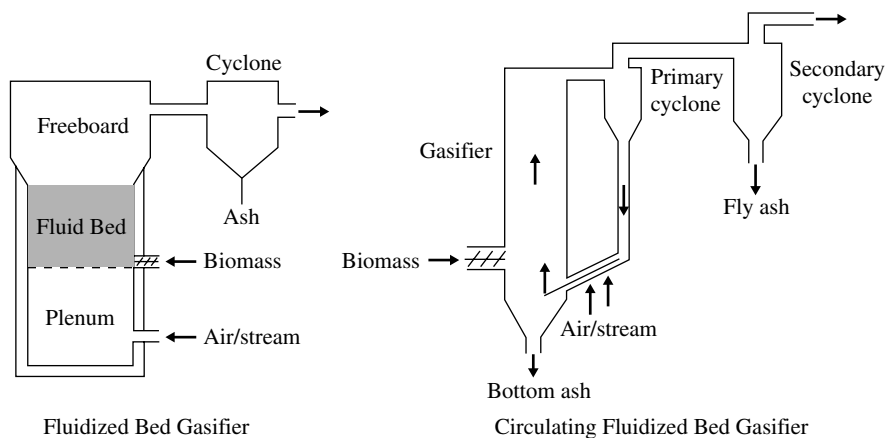
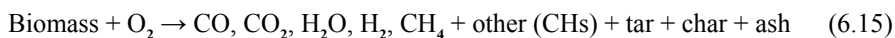


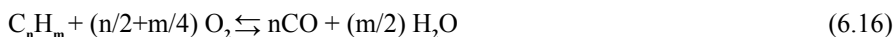
Fig. 6.11 Fluidized-bed and circulating fluidized-bed gasifier systems

tion paths. While the reactions that take place in a gasifier are complex, they can be categorized as follows: flash evaporation of inherent moisture, devolatilization of higher organics, heavy hydrocarbon cracking, pyrolysis, and steam reforming.

Most biomass gasification systems utilize air or oxygen in partial oxidation or combustion processes. Volatile matter partially oxidizes to yield the combustion products H_2O and CO_2 , plus heat to continue the endothermic gasification process. A product gas from thermal decomposition is composed of CO , CO_2 , H_2O , H_2 , CH_4 , other gaseous hydrocarbons (CHs), tars, char, inorganic constituents, and ash. Gas composition of product from the biomass gasification depends heavily on the gasification process, the gasifying agent, and the feedstock composition. A generalized reaction describing biomass gasification is as follows:



The relative amount of CO , CO_2 , H_2O , H_2 , and (CHs) depends on the stoichiometry of the gasification process. If air is used as the gasifying agent, then roughly half of the product gas is N_2 . The air/fuel ratio in a gasification process generally ranges from 0.2 to 0.35 and if steam is the gasifying agent, the steam/biomass ratio is around 1. The actual amount of CO , CO_2 , H_2O , H_2 , tars, and (CHs) depends on the partial oxidation of the volatile products, as shown in Eq. 6.15.



Most biomass gasification systems utilize air or oxygen in partial oxidation or combustion processes. These processes suffer from low thermal efficiencies and low Btu gas because of the energy required to evaporate the moisture typically inherent in the biomass and the oxidation of a portion of the feedstock to produce this energy.

The processing of synfuels from biomass will lower the energy cost, improve the waste management and reduce harmful emissions. This triple assault on plant

operating challenges is a proprietary technology that gasifies biomass by reacting it with steam at high temperatures to form a clean-burning syngas. The molecules in the biomass (primarily carbon, hydrogen and oxygen) and the molecules in the steam (hydrogen and oxygen) re-organize to form this syngas.

In essence, the system embodies a fast, continuous process for pyrolyzing or thermally decomposing biomass and steam reforming the resulting constituents. The entire process occurs in a reducing environment, not an oxidizing environment like other biomass gasifiers. While the reactions that take place in the gasifier are complex, they can be categorized as follows: flash evaporation of inherent moisture, devolatilization of higher organics, heavy hydrocarbon cracking, pyrolysis, and steam reforming. The major thermochemical reactions include the following:

Steam and methane:



Water–gas shift:



Carbon char to methane:



Carbon char oxides (Boudouard reaction):

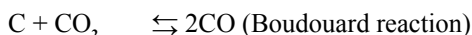


The process is extremely efficient, achieving over 97% conversion of biomass carbon to useful syngas without producing troublesome tars, oils, or contaminated effluents. The process is also quite robust in its ability to handle feedstocks with varying degrees of inherent moisture, ranging from bone-dry wood (in which case moisture is actually added to the feedstock) to organic sludge with moisture contents of over 60%. Unlike traditional partial oxidation systems where any moisture in the feedstock results in an energy efficiency penalty, the process utilizes a portion of the moisture to produce hydrogen and other combustible gases. At 40% moisture in the feedstock, the system achieves a cold gas efficiency of about 80%.

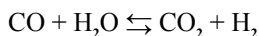
Char gasification is the rate-limiting step in the production of gaseous fuels from biomass. Arrhenius kinetic parameters were determined for the reaction of chars prepared by pyrolysis of cottonwood at 1275 K with steam and carbon dioxide. Results indicate that both reactions are approximately zero order with respect to char; the overall reaction rate is fairly constant throughout and declines only when the char is nearly depleted. This suggests that the reaction rate depends on such factors as total available active surface area or interfacial area between the char and catalyst particles. These parameters would remain relatively constant during the gasification process. Sodium and potassium catalysts were equally effective for the gasification of wood char. The iron and nickel transition metals provided the highest initial catalytic activity, but lost their activity well before the char completely reacted. Softwood and hardwood chars exhibited similar gasification behavior. Results indicate that the mineral (ash) content and composition of the original

biomass material, and pyrolysis conditions under which char is formed significantly influence the char gasification reactivity (Demirbas, 2000).

The char yield in a gasification process can be optimized to maximize carbon conversion or the char can be thermally oxidized to provide heat for the process. Char is partially oxidized or gasified according to the following reactions:



The gasification product gas composition, particularly the H_2 :CO ratio, can be further adjusted by reforming and shift chemistry. Additional hydrogen is formed when CO reacts with excess water vapor according to the water–gas shift reaction:



Carbon chars to methane reaction:



6.5.3.2 Electricity from Cogenerative Biomass Firing Power Plant

The future of modern biomass electricity generation lies in biomass integrated gasification/gas turbine technology, which offers high energy conversion efficiencies. The electricity is produced by direct combustion of biomass, advanced gasification and pyrolysis technologies, which are almost ready for commercial-scale use. Biomass power plants (BPPs) use technology that is very similar to that used in coal-fired power plants. For example, biomass plants use similar steam-turbine generators and fuel delivery systems. BPP efficiencies are about 25%. Electricity costs are in the 6–8 ¢/kWh range. The average BPP is about 20 MW in size, with a few dedicated wood-fired plants in the 40–50 MW range. As the biomass-to-electricity industry grows, it will be characterized by larger facilities of 50–150 MW capacity, with a gas turbine/steam combined cycle. Biomass is burned to produce steam and the steam turns a turbine and drives a generator, producing electricity. Because of potential ash build-up, only certain types of biomass materials are used for direct combustion. Heat is used to thermochemically convert biomass into a pyrolysis oil. The oil, which is easier to store and transport than solid biomass material, is then burned like petroleum to generate electricity.

Biomass can be used as a primary energy source or as a secondary energy source to power gas turbines. As a secondary energy source, biomass is used to make a fuel, which can be used to fire a gas turbine. The heat produced from the electricity generating process is captured and utilized to produce domestic purposes and can be used in steam turbines to generate additional electricity. Co-generation is the simultaneous production of electricity and useful thermal energy from a single source.

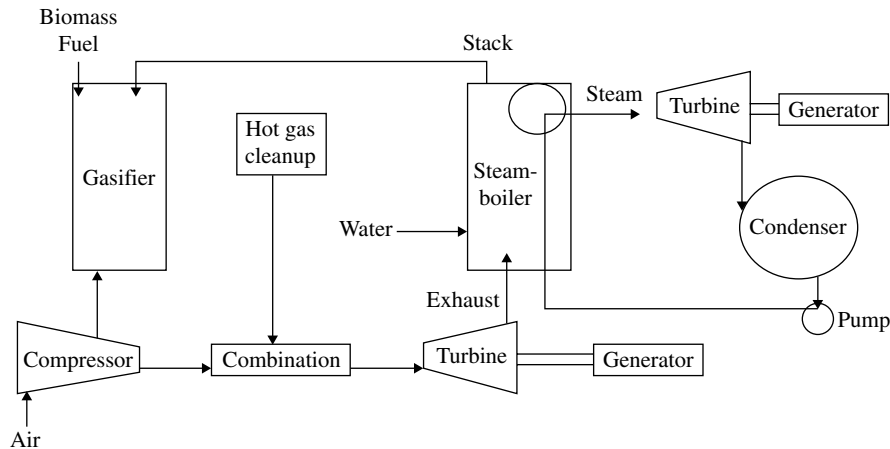


Fig. 6.12 Integrated biomass gas turbine/steam combined-cycle power plant

Practically all biomass-based electricity generation plants employ steam turbine systems. Such electricity generation is established in developed countries in order to upgrade lignocellulosic-based waste materials. Most systems are based on low-pressure boilers (about 20–25 bar) with efficiencies slightly below 20%. Modern biomass-powered high-pressure (60–100 bar) boiler turbine systems produce electricity with efficiencies approaching 32%. Figure 6.12 shows the integrated biomass gas turbine/steam combined-cycle power plant.

6.5.4 *Hydrogen from Biomass via Non-Conventional Processes*

Hydrogen production from gasified biomass by sponge iron reactor is also reported (Nath and Das, 2003). The sponge-iron process (or steam-iron process) offers a simple possibility to store the energy of synthesis gas. Friedrich et al. (1995) worked on the purification of nitrogen-containing reduction gas from a biomass gasifier using wood and wood waste. The process involves two steps:

1. Cleaning of gas from solid biomass or methane



2. Energy storage in sponge iron



The redox process (RP) development was eventually abandoned as other technologies such as pressure swing absorption (PSA) and cryogenic separation began to dominate. In recent years there has been a renewed interest in developing the RP.

In this process dry biomass is fed into a gasifier where it is converted to a combustible fuel gas. On exiting the gasifier the fuel gas temperature was assumed to be 1175 K. The fuel gas then passes through a cyclone to remove entrained char and ash.

The gasifier fuel gas quality is an important issue for the RP development. The effect of the fuel gas composition has been modeled. The modeling showed that the potential hydrogen production efficiency is strongly dependent on the combustion products/syngas (CP/SG) ratio $[(\text{CO}_2 + \text{H}_2\text{O})/(\text{CO} + \text{H}_2) = \text{CP/SG}]$ of the fuel gas.

A core aspect of the model is the determination of the chemical conversion of gasifier SG to hydrogen by the RP. For conditions where steam availability is not limiting, the chemical conversion relates to the difference between the initial and final combustion/fuel ratio of the fuel gas. The initial CP/SG ratio is determined by the gasifier and the biomass feedstock. The final CP/SG ratio is determined by the thermochemical properties of the metal oxide material. Ideally the difference between the initial $(\text{CP/SG})_{\text{initial}}$ and final $(\text{CP/SG})_{\text{final}}$ ratios should be as large as possible. In reality the availability of steam for the re-oxidation of the metal oxide is limiting for conditions where the difference in the CP/SG ratios are large.

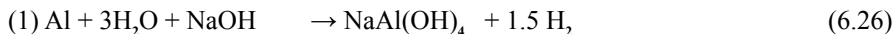
One way to increase the difference between the $(\text{CP/SG})_{\text{initial}}$ and $(\text{CP/SG})_{\text{final}}$ ratios is to increase the $(\text{CP/SG})_{\text{final}}$ ratio by modifying the metal oxide material. This may be achieved by using mixed metal oxides. A goal must be to find the optimum CP/SG ratio. The optimum metal oxide CP/SG ratio depends on the gasifier fuel gas composition.

Hydrogen was produced from organic solid wastes by gasification using solar process heat (Antal et al., 1974). A detailed review with many references of the technology describes solar gasification of carbonaceous materials to produce a syngas quality intermediate for production of hydrogen and other fuels is found in the literature (Yogev et al., 1998; Nath and Das, 2003). Shahbazov and Usupov (1994) have shown good yield of hydrogen from agricultural wastes using a parabolic mirror reflector. The use of a palladium diaphragm in this respect is reported to achieve solar-assisted hydrogen separations from the gases generated by pyrolysis of hazelnut shells at 775–975 K. During the experimental studies, mass loss of hazelnut shells, combustible gas quantities, membrane temperatures in the solar reactor and the amounts of pure hydrogen gas were determined (Midilli et al., 2000). Walcher et al. (1996) have mentioned a plan to utilize agricultural wastes in a heliothermic gasifier.

Several novel heat sources and chemistries have also been explored for hydrogen from organic biomass. Safrany (1971) has proposed the use of a thermonuclear device to vaporize waste organic materials in an underground, large-scale plasma process. In the 1980s, two novel processes for hydrogen from carbonaceous materials were presented (Milne et al., 2002).

Hydrogen can be produced chemically by using sodium hydroxide (NaOH) as a catalyst, and aluminum (Al) and its alloys can react with water to generate hydrogen gas. Although other metals such as zinc and chromium can perform the same reaction, aluminum is among the most promising materials for future development because it is safer and easier to transport than some other hydrogen storage materials like sodium borohydride.

The initial reaction (1) consumes NaOH and produces both hydrogen gas and an aluminate byproduct. Upon reaching its saturation limit, the aluminate compound decomposes (2) into sodium hydroxide and a crystalline precipitate of aluminum hydroxide. This process is similar to the reactions inside an aluminum battery.

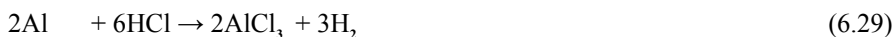


The overall reaction is described by reaction (3).



In this process, aluminum acts as a compact hydrogen storage device because 1 kg of aluminum can theoretically produce up to 0.111 kg of hydrogen (or 11.1%).

Hydrogen also can be produced chemically by using waste hydrochloric acid (HCl) and scrap metal can react with acid to generate hydrogen gas.



6.5.5 Hydrogen from Biomass Gasification by Steam Reforming

Steam reforming or gasification by steam reforming is a method of producing hydrogen-rich gas from carbonaceous biorenewables. Steam reforming process provides the opportunity to convert biorenewable materials into clean fuel gases or syngas ($\text{H}_2 + \text{CO}$). On an industrial scale, it is the dominant method for producing hydrogen. Table 6.8 shows the range of the main operating parameters in pyrolysis and steam gasification processes (Demirbas, 2002b).

Reforming reactions between hydrocarbons and water to generate hydrogen are endothermic, and conventional steam reforming of petroleum thus depends on the combustion of additional hydrocarbons to provide the heat needed to drive the reforming reaction. In contrast, the energy required for the aqueous-phase reforming of oxygenated hydrocarbons may be produced internally, by allowing a fraction of the oxygenated compound to form alkanes through exothermic reaction pathways (Cortright et al., 2002).

In the steam reforming reaction, steam reacts with hydrocarbons in the feed to predominantly produce carbon monoxide and hydrogen, commonly called synthesis gas. Steam reforming can be applied to various solid waste materials including, municipal organic waste, waste soil, sewage sludge, paper mill sludge, black liquor, refuse-derived fuel, and agricultural waste. Steam reforming of natural gas, sometimes referred to as steam methane reforming is the most common method of producing commercial bulk hydrogen. Steam reforming of natural gas is currently

Table 6.8 Range of the main operating parameters in pyrolysis and steam gasification processes

Process	Temp (K)	Heating rate (K/s)	Residence time (s)	Water/biomass
Pyrolysis	675–875	0.1–1	600–2000	0.1–2
Fast pyrolysis	925–1175	250–300	1–3	0.2–0.6
Steam gasification	975–1225	300–500	0.5–2	0.8–2

the least expensive method of producing hydrogen, and used for about half of the world's production of hydrogen (Demirbas, 2008b).

Hydrogen production from carbonaceous solid wastes requires multiple catalytic reaction steps: For the production of high-purity hydrogen, the reforming of fuels is followed by two water–gas shift reaction steps, a final carbon monoxide purification and carbon dioxide removal. Steam reforming, partial oxidation and autothermal reforming of methane are well-developed processes for the production of hydrogen. Stepwise steam reforming of methane for production of carbon monoxide-free hydrogen has been investigated at various process conditions by Choudhary and Goodman (2000). The process consists of two steps involving the decomposition of methane to carbon monoxide-free hydrogen and surface carbon in the first step followed by steam gasification of this surface carbon in the second step. The amount of carbon monoxide-free hydrogen formed in the first step hydrogen is produced in the second step of the reaction. The mixture of gases (primarily CH_4 and CO_2) can be separated or simply methanated and returned to the first step (Choudhary and Goodman, 1999).

Steam, at high temperatures (975–1375 K) is mixed with methane gas in a reactor with a Ni-based catalyst at pressures of 3–25 bar to yield carbon monoxide (CO) and hydrogen (H_2). Steam reforming is the process by which methane and other hydrocarbons in natural gas are converted into hydrogen and carbon monoxide by reaction with steam over a nickel catalyst on a ceramic support. The hydrogen and carbon monoxide are used as initial material for other industrial processes.



It is usually followed by the shift reaction:

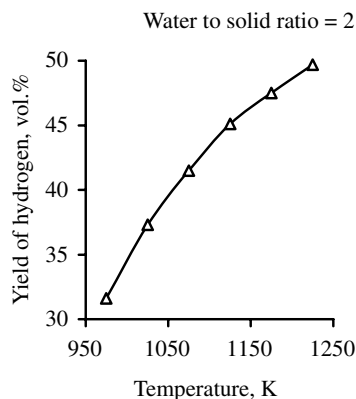


The theoretical percentage of hydrogen to water is 50%. The further chemical reactions for most hydrocarbons that take place are:



It is possible to increase the efficiency to over 85% with an economic profit at higher thermal integration. There are two types of steam reformers for small-scale hydrogen production: conventional reduced-scale reformers and specially designed reformers for fuel cells.

Fig. 6.13 Yield of hydrogen of beech wood by steam reforming at different temperatures



Commercial catalysts consist essentially of Ni supported on α -alumina. Mg-promoted catalysts showed a greater difficulty for Ni precursor's reduction besides different probe molecules (H_2 and CO) adsorbed states. In the conversion of cyclohexane, Mg inhibited the formation of hydrogenolysis products. Nonetheless, the presence of Ca did not influence the metallic phase. The impregnated Ni/MgO-catalyst performed better than the other types (Santos et al., 2004).

Figure 6.13 shows the yield of hydrogen of beech wood gasification by steam reforming at different temperatures (Demirbas, unpublished). The yields of hydrogen from beech wood gasification by steam reforming increase from 31.6 to 47.9% for (water/solid)=1 and from 31.6 to 49.7% for (water/solid)=2 (Fig. 6.13) with increasing of temperature from 975 to 1225 K.

Cox et al. (1995) portray a new approach to thermochemical gasification of biomass to hydrogen. The process is based on catalytic steam gasification of biomass with concurrent separation of hydrogen in a membrane reactor that employs a permselective membrane to separate the hydrogen as it is produced. The process is particularly well-suited for wet biomass and may be conducted at temperatures as low as 575 K.

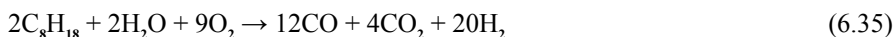
A study of almond shell steam gasification in a fluidized bed revealed that, over the range 775 to 1075 K, smaller particle size yielded more hydrogen than did higher temperatures (Rapagna, 1996). The catalytic converter, using different steam reforming nickel catalysts and dolomite, was tested over a range of 933 to 1103 K. Fresh catalyst at the highest temperature yielded 60% by volume of hydrogen (Rapagna and Foscolo, 1998).

6.5.6 Hydrogen from Biomass via Air–Steam Gasification

The air–steam gasification would be one of the practical conversion technologies among biomass gasification (Li et al., 2004). In general, the gasification tempera-

ture is higher than that of pyrolysis and the yield of hydrogen from the gasification is higher than that of the pyrolysis.

Partial oxidation of hydrocarbons is the exothermic reaction with oxygen and steam. The amounts of oxygen and water vapor are controlled so that the reaction proceeds without the need for external energy. An example reaction for this process is:



The carbon dioxide from the gas mixture is removed by washing with water and the carbon monoxide is removed by absorption or membrane separation.

Yields of hydrogen of hazelnut shell, tea waste and spruce wood samples by air–steam gasification at different temperatures are given in Figs. 6.13 to 6.15, respectively (Demirbas, unpublished work). As can be seen in Fig. 6.13, the percentage of hydrogen in the gaseous products from the samples of hazelnut shell increased from 43.3 to 56.9% by volume, respectively, while the final air–steam gasification temperature was increased from 900 to 1250 K. The hydrogen yields were 43.3, 47.3, 50.4, 52.5, 54.0, 55.4, 56.2 and 56.9% by volume for 900, 950, 1000, 1050, 1100, 1150, 1200 and 1250 K, respectively.

The percentage of hydrogen in gaseous products from the samples of hazelnut shell, tea waste and spruce wood increased from 43.3 to 56.9%, 41.0 to 53.9% and 40.0 to 51.5% by volume, respectively, while the final air–steam gasification temperature was increased from 900 to 1250 K (Figs. 6.14 to 6.16).

Comparison of pyrolysis and air–steam gasification shows that the yield of hydrogen from biomass is generally higher by air–steam gasification than that by pyrolysis, because with interaction of water and char from decomposition of biomass intermediate products are formed, which leads to more hydrogen-rich gas yield by the steam reforming.

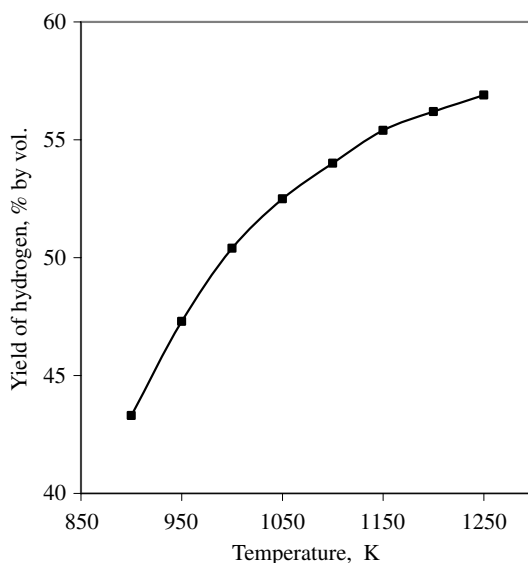


Fig. 6.14 Hydrogen yield of hazelnut shell by air–steam gasification at different temperatures

Fig. 6.15 Yield of hydrogen of tea waste by air–steam gasification at different temperatures

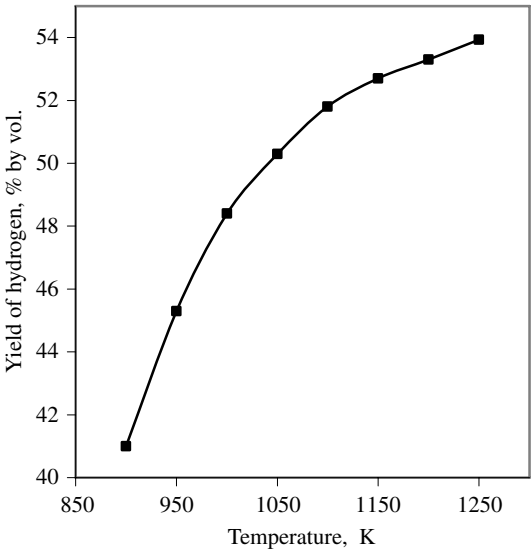
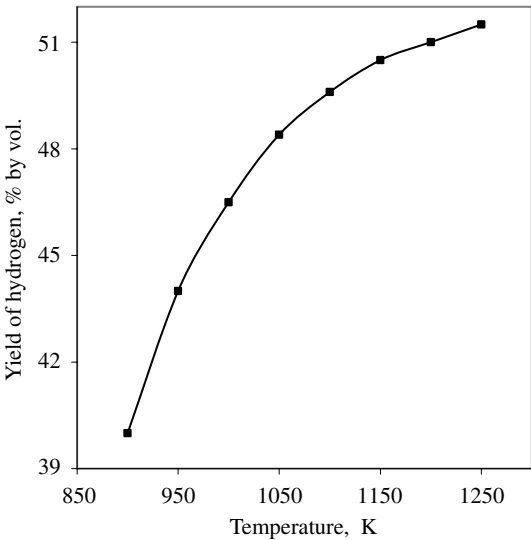


Fig. 6.16 Hydrogen yield of spruce wood by air–steam gasification at different temperatures



The effect of biomass structural components (i.e., hemicelluloses, cellulose and lignin) on air–steam gasification was considerably important by comparison with the experimental results and the structural components given in Table 6.2. From the results, the product gas composition was highly dependent on hemicelluloses and lignin contents of biomass material. The yields of hydrogen in gaseous products from biomass samples by air–steam gasification increase with increasing hemicelluloses and lignin contents.

6.5.7 *Hydrogen from Biomass by Supercritical Water Gasification*

The supercritical fluid extraction (SFE) is a process in which a highly compressed gas (fluid) is brought into contact with a relatively non-volatile solid or liquid at temperatures at or slightly above the critical temperature of the solvent. Under such conditions, the condensed phase will begin to volatilize, which is interpreted as the supercritical fluid phase (Vayisoglu et al., 1996). The SFE is one of the best methods to obtain liquid fuels from coals. The SFE extraction is carried out in an autoclave at above the critical temperature and the pressure of the solvent. The yield of soluble material increases with increasing pressure (Paul and Wise, 1971).

Comparison with other biomass thermochemical gasification such as air gasification or steam gasification, the supercritical water gasification (SCWG) can directly deal with the wet biomass without drying, and has high gasification efficiency in relatively lower temperature. The cost of hydrogen production from supercritical water gasification of wet biomass was several times higher than the current price of hydrogen from steam methane reforming. Biomass is gasified in supercritical water at a series of temperatures and pressures during different resident times and the product gas is composed of H_2 , CO_2 , CO , CH_4 , and a small amount of C_2H_4 and C_2H_6 . Supercritical water is a promising reforming media for the direct production of hydrogen at 875–1075 K temperatures with a short reaction time (2–6 s). As the temperature is increased from 875 to 1075 K the H_2 yield increases from 53 to 73% by volume, respectively. In addition to being a high mass transfer effect, supercritical water also participates in reforming reaction. Pressure has a negligible effect on hydrogen yield above the critical pressure of water (Demirbas, 2004, 2005b).

Hydrogen production by biomass gasification in supercritical water (SCW) is a promising technology for utilizing high moisture content biomass, but reactor plugging is a critical problem for biomass gasification in the tubular reactor. Model compound (glucose) and real biomass (corn cob) were gasified under SCW conditions to generate hydrogen-rich fuel gas and a performance testing of the new SCW fluidized-bed system was conducted. The product gas composed of H_2 , CH_4 , CO_2 , CO and small amount of C_2H_4 and C_2H_6 was obtained. The effects of solution concentration, temperature, pressure and oxidant concentration on gasification were studied. The results showed that using a fluidized-bed reactor for biomass gasification in SCW has many advantages and good prospects (Lu et al. 2008).

Biomass gasification in supercritical water is a promising technology for hydrogen production by utilizing wet biomass, having only been developed in last two decades (Lu et al., 2007). The catalyst shows a destructive effect on the organic compounds and H_2 and CO_2 form at the end of the catalytic steam reforming process. The main advantage of gasification in supercritical water is the high solid conversion, i.e., low levels of char and tars. For wet biomass containing large amounts of water up to 90%, supercritical water gasification (SCWG) appears as a useful technology (Yanik et al., 2007). Biomass energy of low quality can be converted to hydrogen energy of high quality by the SCWG process (Guo et al., 2007).

Products from biomass by supercritical water (SCW) depend on the nature and structure of the biomass. The effects of SCW on the biomass constituents should be separately studied. For example SCW affects unsaturated compounds, and unsaturated fatty and resin acids, rather than those of saturated ones under different reaction conditions (Watanabe et al., 2006). The diffusion or mass transfer rate of SCW into the individual component of biomass has been studied separately (Antal et al., 2000; Feng et al., 2004).



In this idealized, stoichiometric equation (Eq. 6.36), cellulose (represented as $\text{C}_6\text{H}_{10}\text{O}_5$) reacts with water to produce H_2 and CO_2 , the commercial production of H_2 from methane by the catalytic steam reforming process (Wagner and Froment, 1992).

Recently, the supercritical fluid treatment has been considered to be an attractive alternative in science and technology as a chemical reaction field. The molecules in the supercritical fluid have high kinetic energy like the gas and high density like the liquid. Therefore, it is expected that the chemical reactivity can be high. In addition, the ionic product and dielectric constant of supercritical water are important parameters for chemical reaction. Therefore, the supercritical water can be realized from the ionic reaction field to the radical reaction field. For example, the ionic product of the supercritical water can be increased by increasing pressure, and the hydrolysis reaction field is realized. Therefore, the supercritical water is expected as a solvent for converting biomass into valuable substances (Hao et al., 2003).

Especially, the temperature in which the gasification reaction can take place depends on the category and the structure of the biomass greatly. Many reactions in supercritical water gasification have begun when the temperature and the pressure exceeds the critical point of water. In supercritical water gasification, the reaction generally takes place at the temperature over 875 K and a pressure higher than the critical point of water. With temperatures higher than 875 K, water becomes a strong oxidant, and oxygen in water can be transferred to the carbon atoms of the biomass. CO is the primary product in SCWG and it reacts with steam to produce additional H_2 and CO_2 by the water–gas shift reaction. The hydrogen atoms of water and of the biomass are set free and form H_2 . The gas product consists of hydrogen, CO_2 , CH_4 and CO (Antal, 1978).

A problem of general nature in SCGW is the required heat exchange between the reactor outlet and inlet streams. To achieve an acceptable thermal efficiency, it is crucial for the process that the heat of the inlet stream is utilized as far as possible to pre-heat the feedstock stream (mainly water) to reaction conditions. At the same time, heating of the biomass slurry in the inlet tube of a reactor is likely to cause fouling/plugging problems because the thermal decomposition (> 523 K) starts already far below the desired reaction temperature (> 873 K) (Kruse et al., 2000). A schematic diagram of experimental apparatus of supercritical water gasification is depicted in Fig. 6.17. Supercritical water is a promising reforming media for the direct production of hydrogen at 875–1075 K temperatures with a short reaction time between 2 and 6 s. In addition to being a high mass transfer effect, supercritical

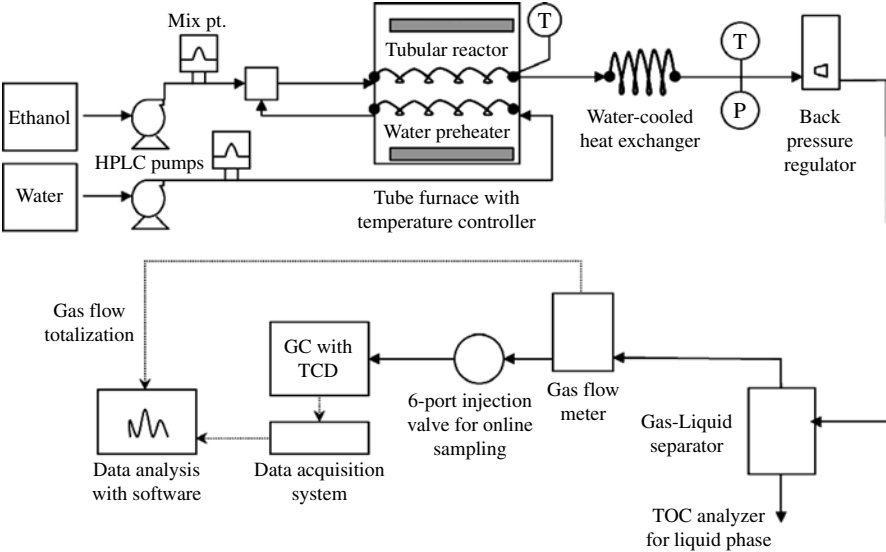


Fig. 6.17 Schematic diagram of experimental apparatus of supercritical water gasification

Table 6.9 Typical product yield (% by vol.) distributions for experiments with and without Ru/Al₂O₃ catalyst at 973 K with 1 wt.% glucose feed (15.9 g of catalyst/g mol of glucose)

	H ₂	CO ₂	CH ₄	CO
Direct reforming	54.5	31.4	8.5	5.6
Catalytic reforming	68.9	29.8	1.3	0.1

water also participates in the reforming reaction. The molecules in the supercritical fluid have high kinetic energy like the gas and high density like the liquid. Therefore, it is expected that the chemical reactivity can be high. In addition, the ionic product and dielectric constant of supercritical water, which are important parameters for chemical reactions, can be continuously controlled by regulating pressure and temperature. Pressure has a negligible effect on the hydrogen yield above the critical pressure of water (Gadhe and Gupta, 2007). As the temperature is increased from 875 to 1075 K the H₂ yield increases from 53 to 73% by volume, respectively. Only a small amount of hydrogen is formed at low temperatures, indicating that direct reformation reaction of ethanol as a model compound in SCW is favored at high temperatures (> 975 K). With an increase in the temperature, the hydrogen and carbon dioxide yields increase, while the methane yield decreases. The water excess leads to a preference for the formation of hydrogen and carbon dioxide instead of carbon monoxide. The formed intermediate carbon monoxide reacts with water to hydrogen and carbon dioxide. The low carbon monoxide yield indicates that the water–gas shift reaction approaches completion (Byrd et al., 2007).

Thermochemical gasification of biomass has been identified as a possible system to produce renewable hydrogen with less dependence on exhaustible fossil energy resources. Compared with other biomass thermochemical gasifications, such as air gasification or steam gasification, the SCWG has high gasification efficiency at lower temperatures and can deal directly with wet biomass without drying (Yan et al., 2006).

The capillaries (1 mm ID and 150 mm length tubular reactors) are heated rapidly (within 5 s) in a fluidized sand bed to the desired reaction temperature. Experimentation with the batch capillary method has revealed that, especially at low temperatures and high feed concentrations, char formation occurs. A fluidized-bed reactor might be a good alternative to solve the problems related to this char and ash formation (Kruse et al., 2000).

To study the effect of the $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst on hydrogen yield for reforming of glucose in supercritical water, the experiments were compared to reactions with and without catalytic runs under identical conditions. Typical product distributions are shown in Table 6.9 for experiments with and without a $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst at 973 K with 1 wt.% glucose feed (Byrd et al., 2007). There was a significant reduction in carbon monoxide and methane yields in the presence of the catalyst. The main products of the reaction were hydrogen, methane, carbon dioxide, and carbon monoxide. The low carbon monoxide yield (0.1% by vol.) indicates that the water–gas shift reaction approaches completion.

Cellulose and sawdust were gasified in supercritical water to produce hydrogen-rich gas, and Ru/C , Pd/C , CeO_2 particles, nano- CeO_2 and nano- $(\text{CeZr})_x\text{O}_2$ were selected as catalysts. The experimental results showed that the catalytic activities were $\text{Ru}/\text{C} > \text{Pd}/\text{C} > \text{nano-}(\text{CeZr})_x\text{O}_2 > \text{nano-}\text{CeO}_2 > \text{CeO}_2$ particle in turn. The 10 wt.% cellulose or sawdust with CMC can be gasified almost completely with a Ru/C catalyst to produce 2–4 g hydrogen yield and 11–15 g potential hydrogen yield per 100 g feedstock at the condition of 773 K, 27 MPa, 20 min residence time in supercritical water (Hao et al., 2005).

Catalysts for low-temperature gasification include combinations of stable metals, such as ruthenium or nickel bimetallics and stable supports, such as certain titania, zirconia, or carbon. Without catalyst the gasification is limited (Kruse et al., 2000). Sodium carbonate is effective in increasing the gasification efficiency of cellulose (Minowa et al., 1997). Likewise, homogeneous, alkali catalysts have been employed for high-temperature supercritical water gasification.

The yields of hydrogen from steam gasification increase from 29 to 45% for $(\text{water}/\text{solid})=1$ and from 29 to 47% for $(\text{water}/\text{solid})=2$ with increasing of temperature from 975 to 1225 K. Figure 6.18 shows comparisons for the yield of hydrogen from supercritical fluid extraction (SFE), pyrolysis and steam gasification ($\text{water}/\text{solid}=2$) of beech wood at different temperatures. Distilled water was used in the SFE (the critical temperature of pure water is 647.7 K). From Fig. 6.18, the yield of hydrogen from SFE was considerably high (49%) at lower temperatures. The pyrolysis was carried out at moderate temperatures and steam gasification at the highest temperatures (Demirbas, 2006a).

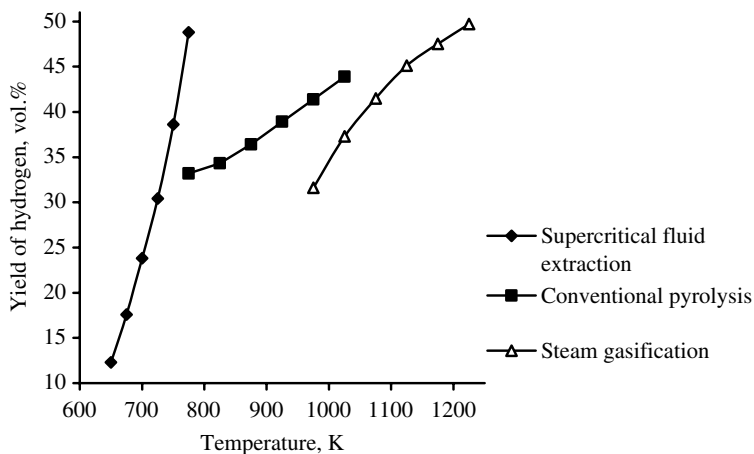


Fig. 6.18 Plots for yield of hydrogen from supercritical fluid (water) extraction, pyrolysis and steam gasification (water/solid=2) of beech wood at different temperatures

6.5.7.1 Advantages of Supercritical Water

The reforming in supercritical water (SCW) offers several advantages over the conventional technologies because of the unusual properties of supercritical water. The density of supercritical water is higher than that of steam, which results in a high space-time yield. The higher thermal conductivity and specific heat of supercritical water is beneficial for carrying out the endothermic reforming reactions (Gadhe and Gupta, 2007). In the supercritical region, the dielectric constant of water is much lower. Further, the number of hydrogen bonds is much smaller and their strength is considerably weaker. As a result, SCW behaves as an organic solvent and exhibits extraordinary solubility toward organic compounds containing large non-polar groups and most permanent gases (Demirbas, 1998; Byrd et al., 2007). Another advantage of SCW reforming is that the H_2 is produced at a high pressure, which can be stored directly, thus avoiding the large energy expenditures associated with its compression. The SCWG process becomes economical as the compression work is reduced owing to the low compressibility of liquid feed when compared to that of gaseous H_2 (Byrd et al., 2007).

6.5.8 Hydrogen-rich Gas from Shells via Supercritical Water Extraction

Agricultural shell samples (walnut, almond, hazelnut cotton cocoon, and sunflower shells) were subjected to supercritical water extraction for producing hydrogen-rich gas mixtures (Demirbas, 2004). Table 6.10 shows structural analysis results of the shell samples. In a typical run of this study, the autoclave was loaded with a 5.0 g

sample and 50–70 g of deionized water. The supercritical fluids extraction (SFE) parameters were adjusted as follows: the temperatures for supercritical water runs were 650 ± 3 , 670 ± 3 , 690 ± 3 , 710 ± 3 , 730 ± 3 and 750 ± 3 K, and pressures measured were 23.2, 25.4, 28.0, 32.5 and 38.7 MPa.

Figure 6.19 shows the plots for yields of hydrogen from supercritical water extraction of shell samples versus temperature. The yields of hydrogen from supercritical water extraction increase with increasing extraction temperatures. The yield of hydrogen from almond shell increases from 6.7 to 13.5% with the temperature increase from 650 to 750 K, respectively (Demirbas, 2004).

Figure 6.20 shows the plots for yields of hydrogen from supercritical water extraction of shell samples versus cellulose content at different temperatures. The yields of hydrogen from supercritical water extraction increase with increasing cellulose contents of the shell samples (Demirbas, 2004).

Table 6.10 Structural analyses results of shell samples (wt.% of dry, ash and extractive-free basis)

Sample of shell	Hemicellulose	Cellulose	Lignin
Almond	29.6 ± 2.8	52.0 ± 5.6	20.9 ± 2.1
Cotton cocoon	10.5 ± 1.1	33.5 ± 3.5	50.0 ± 5.3
Hazelnut	31.4 ± 3.2	27.7 ± 2.9	44.4 ± 4.7
Sunflower	35.6 ± 3.8	49.7 ± 5.2	17.5 ± 1.9
Walnut	22.7 ± 2.3	26.3 ± 2.8	53.8 ± 5.7

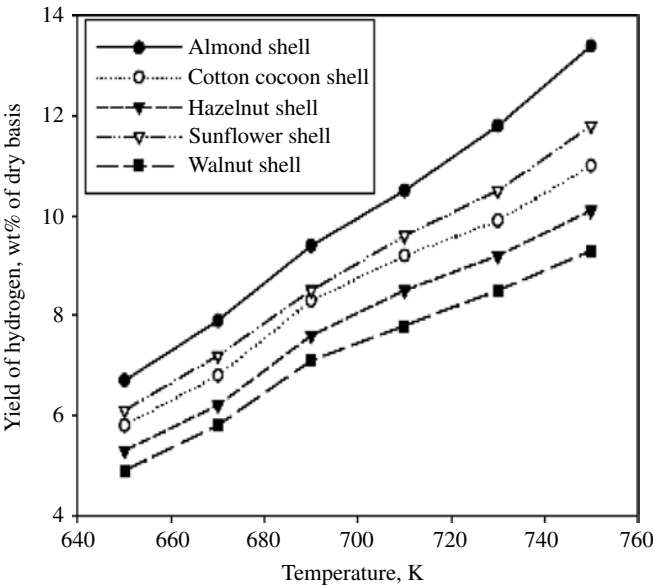


Fig. 6.19 Plots for yields of hydrogen from supercritical water extraction of shell samples versus temperature

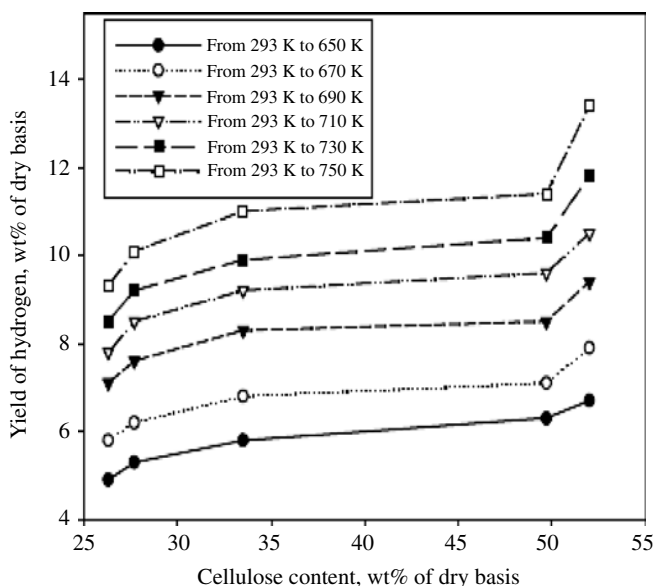


Fig. 6.20 Plots for yields of hydrogen from supercritical water extraction of shell samples versus cellulose content at different temperatures

6.5.9 Production of Hydrogen from Mosses and Algae via Pyrolysis and Steam Gasification

Most studies concerning mosses have been taxonomic and medical. Some species of Bryophytes, such as *Atricum*, *Dicranum*, *Mnium*, *Polytrichum*, and *Sphagnum*, are important for the economy. Approximately 200 million tons of peat formed from *Sphagnum* per year is used as a fuel in the world (Cetin and Yurdakulol, 1985, 1988). The chemical compositions of algae are given in Table 6.11 (Demirbas, 2007). Algae were mainly composed of proteins, lipids and water-soluble carbohydrates.

Two moss samples (*Polytrichum commune*, *Thuidium tamariscinum*), one alga sample (*Cladophora fracta*), and one microalga sample (*Chlorella protothecoides*) were subjected to pyrolysis and steam gasification for producing hydrogen-rich gas (Demirbas, unpublished work).

The temperature of the reaction vessel was measured with an iron-constantan thermocouple and controlled at ± 3 K. The pyrolysis experiments were performed at temperatures of 575, 625, 675, 725, 775, 825 and 925 K. The steam gasification experiments were carried out at temperatures of 825, 875, 925, 975, 1025, 1075, 1125, 1175 and 1225 K (Demirbas, unpublished work).

Table 6.12 shows the proximate analysis data and higher heating values (HHV) of samples. The HHV (MJ/kg) of the moss and alga samples as a function of fixed carbon (FC), wt.% can be calculated from:

$$\text{HHV} = 0.322 (\text{FC}) + 10.7123 \quad (6.37)$$

Table 6.11 Chemical compositions of algae on a dry matter basis (%)

Species of sample	Proteins	Carbohydrates	Lipids	Nucleic acid
<i>Scenedesmus obliquus</i>	50–56	10–17	12–14	3–6
<i>Scenedesmus quadricauda</i>	47	–	1.9	–
<i>Scenedesmus dimorphus</i>	8–18	21–52	16–40	–
<i>Chlamydomonas reinhardtii</i>	48	17	21	–
<i>Chlorella vulgaris</i>	51–58	12–17	14–22	4–5
<i>Chlorella pyrenoidosa</i>	57	26	2	–
<i>Spirogyra</i> sp.	6–20	33–64	11–21	–
<i>Dunaliella bioculata</i>	49	4	8	–
<i>Dunaliella salina</i>	57	32	6	–
<i>Euglena gracilis</i>	39–61	14–18	14–20	–
<i>Prymnesium parvum</i>	28–45	25–33	22–38	1–2
<i>Tetraselmis maculata</i>	52	15	3	–
<i>Porphyridium cruentum</i>	28–39	40–57	9–14	–
<i>Spirulina platensis</i>	46–63	8–14	4–9	2–5
<i>Spirulina maxima</i>	60–71	13–16	6–7	3–4.5
<i>Synechococcus</i> sp.	63	15	11	5
<i>Anabaena cylindrica</i>	43–56	25–30	4–7	–

Table 6.12 Proximate analysis data and higher heating values (HHV) of samples (wt.% dry basis)

Sample	Fixed carbon	Volatile matter	Ash	HHV (MJ/kg)
<i>Polytrichum commune</i>	19.4	65.8	14.8	17.0
<i>Thuidium tamarascinum</i>	15.4	72.3	12.3	15.5
<i>Cladophora fracta</i>	28.1	65.6	6.3	19.8
<i>Chlorella protothecoides</i>	39.6	54.6	5.8	23.6

The HHVs can be calculated using Eq. 6.37 and represent high correlation obtained by means of regression analysis. The correlation coefficient r is 0.999.

The yields of bio-oil from the samples via pyrolysis are presented as a function of the temperature (K) in Fig. 6.21. The yield of bio-oil from pyrolysis of the samples increased with temperature, as expected. The yields were increased up to 750 K in order to reach the plateau values at 775 K. The maximum yields for *Polytrichum commune*, *Thuidium tamarascinum*, *Cladophora fracta* and *Chlorella protothecoides* were 31.6, 37.3, 45.0 and 50.8% of the sample at 925 K, respectively. The bio-oil yields of pyrolysis from algae were higher than those of mosses. Bio-

Fig. 6.21 Plots for yield of bio-oil from moss and alga samples by pyrolysis at different temperatures (K). *Polytrichum commune* (PC), *Thuidium tamarascinum* (TT), *Cladophora fracta* (CF), and *Chlorella protothecoides* (CP)

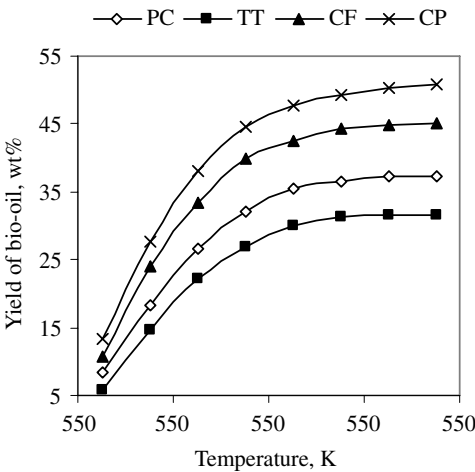
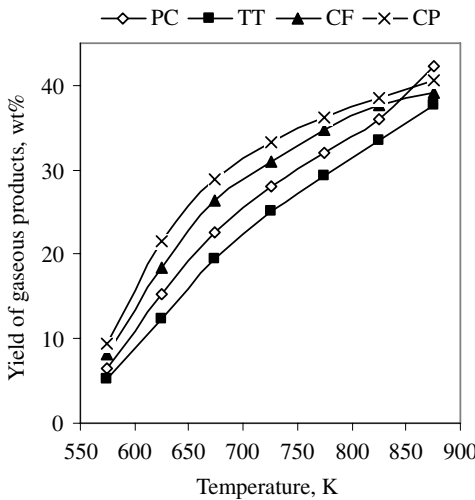


Fig. 6.22 Plots for yields of gaseous products from the samples by pyrolysis. *Polytrichum commune* (PC), *Thuidium tamarascinum* (TT), *Cladophora fracta* (CF), and *Chlorella protothecoides* (CP)



oil comparable to fossil oil was obtained from microalgae (Miao and Wu, 2004). In the pyrolysis process, the yield of charcoal decreases with increasing pyrolysis temperature. The yield of the liquid product is highly excessive at temperatures between 625 and 725 K.

The HHVs for bio-oils from mosses 21.5–24.8 MJ/kg and the HHVs for bio-oils from alga and microalga 32.5 and 39.7 MJ/kg, respectively, were obtained by pyrolysis at temperatures ranging from 775 to 825 K. In general, algae bio-oils are higher quality than bio-oils from mosses.

Figure 6.22 shows the effect of temperature on yields of gaseous products from the samples by pyrolysis. As can be seen in Fig. 6.22, the yields of gaseous products from the samples of *Polytrichum commune*, *Thuidium tamarascinum*, *Cladophora fracta* and *Chlorella protothecoides* increased from 5.3 to 40.6%, 6.5 to 42.2%, 8.2

Fig. 6.23 Plots for yields of hydrogen in gaseous products from the samples by pyrolysis. *Polytrichum commune* (PC), *Thuidium tamarascinum* (TT), *Cladophora fracta* (CF), and *Chlorella protothecoides* (CP)

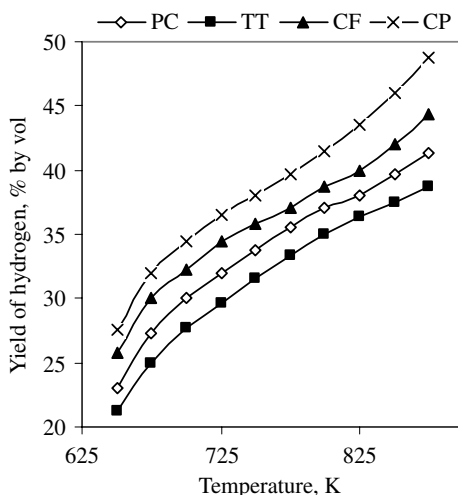
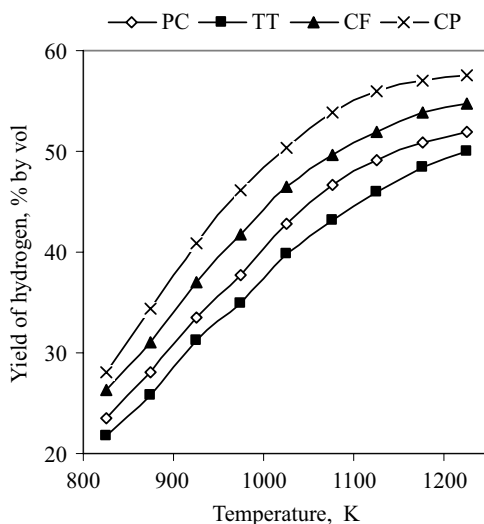


Fig. 6.24 Plots for yields of hydrogen in gaseous products from the samples by steam gasification. *Polytrichum commune* (PC), *Thuidium tamarascinum* (TT), *Cladophora fracta* (CF), and *Chlorella protothecoides* (CP)



to 39.2% and 9.5 to 40.6% by volume, respectively, while the final pyrolysis temperature was increased from 575 to 875 K.

Figure 6.23 shows the plots for yields of hydrogen in gaseous products from the samples by pyrolysis. The percentage of hydrogen in gaseous products from the samples of *Polytrichum commune*, *Thuidium tamarascinum*, *Cladophora fracta* and *Chlorella protothecoides* increased from 21.3 to 38.7%, 23.0 to 41.3% and 25.8 to 44.4% and 27.6 to 48.7% by volume, respectively, while the final pyrolysis temperature was increased from 650 to 875 K.

Figure 6.24 shows the plots for yields of hydrogen in gaseous products from the samples by steam gasification. The percentage of hydrogen in gaseous products from the above-mentioned samples increased from 21.8 to 50.0%, 23.5 to 52.0%,

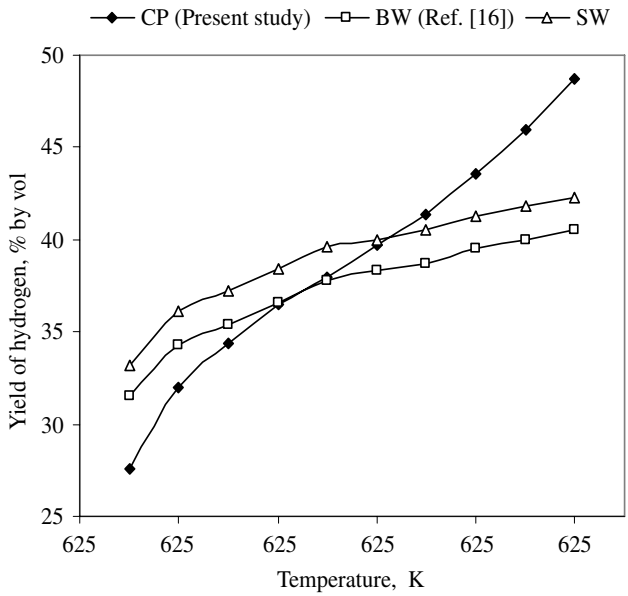


Fig. 6.25 Plots for yields of hydrogen in gaseous products from microalga and wood samples by pyrolysis. *Chlorella protothecoides* (CP), beech wood (BW) and spruce wood (SW)

26.3 to 54.7% and 28.1 to 57.6% by volume, respectively, while the final gasification temperature was increased from 825 to 1225 K.

Figure 6.25 shows the yields of hydrogen in gaseous products from microalga and wood samples by pyrolysis. The hydrogen in gaseous products from the samples of beech wood and spruce wood increased from 31.5 to 40.5% and 33.3 to 42.3% by volume, respectively, while the final pyrolysis temperature was increased from 650 to 875 K (Demirbas and Arin, 2004). Microalgae gaseous products are higher quality than gaseous products from wood (Fig. 6.25). In general, algae gaseous products are higher quality than gaseous products from mosses.

Table 6.13 shows the yields of bio-oil by pyrolysis from moss and alga samples (Demirbas, 2006b). As can be seen from Table 6.13, the bio-oil yield for *Chlorella protothecoides* (a microalga sample) rose from 12.8 to 55.3% as the temperature rose from 575 to 775 K, and then gradually the percentage decreased to 51.8%, obtained at 875 K with a heating rate of 10 K/s. The bio-oil yield for *Polytrichum commune* (a moss sample) rose from 10.3 to 39.1% as the temperature rose from 575 to 775 K, and then decreased to 36.7% obtained at 875 K with a heating rate of 10 K/s (Demirbas, 2006b). For alga, maximum bio-oil yields of between 48.2 and 46.8%, and for microalga 55.3 and 53.7% were obtained at temperatures ranging from 775 to 825 K, whereas for wood, cotton stalk, tobacco stalk and sunflower bagasse, maximum oil yields between 39.7 and 49.4% were obtained at temperatures in the range from 775 to 825 K (Putun, 2002; Gercel, 2002).

Table 6.13 Yields of bio-oil by pyrolysis from moss and alga samples at different temperatures (K)

Sample	575	625	675	725	775	825	875
<i>Polytrichum commune</i>	10.3	20.0	27.5	35.8	39.1	38.4	36.7
<i>Dicranum scoparium</i>	6.0	15.5	21.8	30.7	34.3	33.8	31.7
<i>Thuidium tamarascinum</i>	5.6	14.2	20.7	29.5	33.6	33.4	31.3
<i>Sphagnum palustre</i>	7.9	17.7	25.3	33.5	37.0	36.3	34.6
<i>Drepanocladus revolvens</i>	6.7	16.4	23.5	31.7	35.4	34.7	32.9
<i>Cladophora fracta</i>	10.5	23.5	33.2	43.4	48.2	46.8	44.6
<i>Chlorella protothecoides</i>	12.8	27.4	38.4	50.2	55.3	53.7	51.6

Table 6.14 Yields of gaseous product by pyrolysis from moss and alga samples at different temperatures (K)

Sample	575	625	675	725	775	825	875
<i>Polytrichum commune</i>	6.5	14.8	22.6	26.4	29.2	36.6	42.2
<i>Dicranum scoparium</i>	5.8	12.5	19.8	25.0	27.6	35.0	40.8
<i>Thuidium tamarascinum</i>	5.3	11.2	17.9	23.5	25.6	33.2	39.3
<i>Sphagnum palustre</i>	5.5	11.9	18.3	24.2	26.5	34.0	39.8
<i>Drepanocladus revolvens</i>	5.6	12.3	18.9	24.7	27.0	34.5	40.4
<i>Cladophora fracta</i>	8.2	19.7	28.2	32.6	35.7	38.0	39.7
<i>Chlorella protothecoides</i>	9.5	21.8	29.5	33.7	36.3	38.1	39.5

Table 6.14 shows the yields of gaseous product by pyrolysis from moss and alga samples (Demirbas, 2006b). From Table 6.14, the yields of gaseous products for *Chlorella protothecoides* increased from 9.5 to 39.5% as the temperature rose from 575 to 875 K. The char yields of pyrolysis from mosses were higher than those of algae.

With the interaction of water and char from decomposition of biomass, intermediate products are known to occur which leads to more hydrogen-rich gas yield by the steam reforming process. The pyrolysis was carried out at the moderate temperatures and steam gasification at the highest temperatures. In order to clarify the steam gasification mechanism in detail, more kinetic study is necessary. These results suggest that fundamental information obtained in the gasification of each component could possibly be used to predict the composition of product gas generated in air–steam gasification of biomass.

Summary

Biohydrogen is a renewable biofuel produced from biorenewable feedstocks by a variety of methods, including chemical, thermochemical, biological, biochemical, and biophotolytical methods. The topic of biohydrogen touches on energy security, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sectors of all countries in the world. It is also an environmentally friendly alternative automotive fuel that can be used in an internal combustion engine.

There are three types of microorganisms that produce hydrogen: cyanobacteria, anaerobic bacteria, and fermentative bacteria. The cyanobacteria directly decompose water to hydrogen and oxygen in the presence of light by photosynthesis. Photosynthetic bacteria use organic substrates like organic acids, whereas anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into hydrogen. A promising method is the biological production of hydrogen by fermentation. Fermentative hydrogen production is the fermentative conversion of organic substrates to biohydrogen. This process is manifested by a diverse group of bacteria using multienzyme systems involving three steps similar to anaerobic conversion.

Hydrogen can be produced from biorenewable feedstocks via thermochemical conversion processes such as pyrolysis, gasification, steam gasification, steam reforming of bio-oils, and supercritical water gasification (SWG) of biomass.

Comparison with other biomass thermochemical gasification such as air gasification or steam gasification, the supercritical water gasification (SCWG) can directly deal with the wet biomass without drying, and has high gasification efficiency in relatively lower temperatures. The cost of hydrogen production from supercritical water gasification of wet biomass was several times higher than the current price of hydrogen from steam methane reforming. Biomass is gasified in supercritical water at a series of temperatures and pressures during different resident times and the product gas is composed of H_2 , CO_2 , CO , CH_4 , and a small amount of C_2H_4 and C_2H_6 .

References

- Adams, M.W.W. 1990. The structure and mechanism of iron-hydrogenases. *Biochim Biophys Acta* 1020:115–145.
- Aiba, S., Humphrey, A.E., Milis, N.F. 1973. *Biochemical engineering*, 2nd edn. Academic, New York.
- Akkerman, I., Janssen, M., Rocha, J., Wijffels, R.H. 2002. Photobiological hydrogen production: photochemical efficiency and bioreactor design. *Int J Hydrogen Energy* 27:1195–1208.
- Aoyama, K., Uemura, I., Miyake, J., Asada, Y. 1987. Fermentative metabolism to produce hydrogen gas and organic compounds in a cyanobacterium *Spirulina platensis*. *J Ferment Bioeng* 83:17–20.
- Antal, M.J. 1978. Tower power: producing fuels from solar energy, *in* *Toward a solar civilization*, R.H. Williams (Ed.) MIT Press, Cambridge, MA.

- Antal, M.J., Feber, R.C., Tinkle, M.C. 1974. Proceedings 1st World Hydrogen Energy Conference, Miami Beach, FL.
- Antal, M.J., Allen, S., Schulman, D., Xu, X., Divilio, R. 2000. Biomass gasification in supercritical water. *Ind Chem Eng Res* 39:4040–4053.
- Antal, T.K., Lindblad, P. 2005. Production of H_2 by sulphur-deprived cells of the unicellular cyanobacteria *Gloeocapsa alpicola* and *Synechocystis sp.* PCC 6803 during dark incubation with methane or at various extracellular pH. *J Appl Microbiol* 98:114–120.
- Backman, R., Fredrick, W.J., Hupa, M. 1993. Basic studies on black-liquor pyrolysis and char gasification. *Biores Technol* 46:153–158.
- Benemann, J.R. 1996. Hydrogen biotechnology: progress and prospects. *Nature Biotechnol* 14:1101–1103.
- Benemann, J.R. 1997. Feasibility analysis of photobiological hydrogen production. *Int J Hydrogen Energy* 22:979–987.
- Benemann, J.R. 1998. The technology of biohydrogen. Plenum, New York.
- Benemann, J.R., Weare, N.M. 1974. Hydrogen evolution by nitrogen-fixing. *Anabaena cylindrica* cultures. *Science* 184:174–175.
- Byrd, A.J., Pant, K.K., Gupta, R.B. 2007. Hydrogen production from glucose using Ru/Al_2O_3 catalyst in supercritical water. *Ind Eng Chem Res* 46:3574–3579.
- Caglar, A., Demirbas, A. 2002a. Hydrogen-rich gas mixture from olive husk via pyrolysis. *Energy Convers Manage* 43:109–117.
- Caglar, A., Demirbas, A. 2002b. Conversion cotton cocoon shell to hydrogen-rich gaseous products by pyrolysis. *Energy Convers Manage* 43:489–497.
- Cetin, B., Yurdakulol, E. 1985. Gereke-Aktas (Bolu) ormanlarinin karayosunlari (Musci) florasi. *Doga Bilim Der* 9:29–38 (in Turkish).
- Cetin, B., Yurdakulol, E. 1988. Yedigoller milli parkinin karayosunu florasi. *Turkish J Bot* 12:128–146 (in Turkish).
- Chen, G., Spliethoff, H., Yang, L.B., Andries, J. 2003. Hydrogen production from gasification: pyrolysis of biomass. III. International Slovak Biomass Forum, Bratislava, Slovakia, 3–4 Feb 2003.
- Chornet, E. 2001. Biomass to hydrogen via fast pyrolysis and catalytic steam reforming. Proceedings of the 2001 USA. DOE Hydrogen Program Review (NREL/CP 570-30535).
- Claassen, P.A.M., Lier, J.B.V., Lopez, C.A.M., Niel, E.W.J., Sijtsma, L., Stams, A.J.M., Vriess, S.S.D., Weusthuis, R.A. 1999. Utilization of biomass for the supply of energy carries. *Appl Microbiol Biotechnol* 52:741–755.
- Cortright, R.D., Davda, R.R., Dumesic, J.A. 2002. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* 418:964–967.
- Cox, J.L., Tonkovich, A.Y., Elliott, D.C., Baker, E.G., Hoffman, E.J. 1995. Hydrogen from biomass: a fresh approach. Proceedings of the 2nd Biomass Conference of the Americas (NREL/CP-200-8098; CONF-9508104) August 1995, Portland, Oregon.
- Czernik, S., French, R., Feik, C., Chornet, E. 2001. Production of hydrogen from biomass derived liquids. Proceedings of the 2001 USA. DOE Hydrogen Program Review (NREL/CP 570-30535).
- Das, D., Veziroglu, T.N. 2008. Advances in biological hydrogen production processes. *Int J Hydrogen Energy* 33:6046–6057.
- Demirbas, A. 1998. Yields of oil products from thermochemical biomass conversion processes. *Energy Convers Manage* 39:685–690.
- Demirbas, A. 2000. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Convers Manage* 41:633–646.
- Demirbas, A. 2001. Yields of hydrogen of gaseous products via pyrolysis from selected biomass samples. *Fuel* 80:1885–1891.
- Demirbas, A. 2002a. Gaseous products from biomass by pyrolysis and gasification: effects of catalyst on hydrogen yield. *Energy Convers Manage* 43:897–909.
- Demirbas, A. 2002b. Hydrogen production from biomass by gasification process. *Energy Sources* 24:59–68.

- Demirbas, A. 2004. Hydrogen-rich gas from fruit shells via supercritical water extraction. *Int J Hydrogen Energy* 29:1237–1243.
- Demirbas, A. 2005a. Hydrogen production via pyrolytic degradation of agricultural residues. *Energy Sources* 27:769–775.
- Demirbas, A. 2005b. Hydrogen production from biomass via supercritical water extraction. *Energy Sources* 27:1409–1417.
- Demirbas, M.F. 2006a. Hydrogen from various biomass species via pyrolysis and steam gasification processes. *Energy Sources Part A* 28:245–252.
- Demirbas, A. 2006b. Oily products from mosses and algae via pyrolysis. *Energy Sources Part A* 28:933–940.
- Demirbas, A. 2007. Production of biofuels from macroalgae and microalgae. *Energy Edu Sci Technol* 18:59–65.
- Demirbas, A. 2008a. Biohydrogen generation from organic wastes. *Energy Sources Part A* 30:475–482.
- Demirbas, A. 2008b. Hydrogen production from carbonaceous solid wastes by steam reforming. *Energy Sources Part A* 30:924–931.
- Demirbas, A., Arin, G. 2004. Hydrogen from biomass via pyrolysis: relationships between yield of hydrogen and temperature. *Energy Sources* 26:1061–1069.
- Demirbas, A., Karslioglu, S., Ayas A. 1996. Hydrogen resources: conversion of black liquor to hydrogen-rich gaseous products. *Fuel Sci Technol Int* 14:451–465.
- Demirbas A., Caglar, A. 1998. Catalytic reforming of biomass and heavy oil residues to hydrogen. *Energy Edu Sci Technol* 1:45–52.
- Demirbas, A., Arin, G. 2004. Hydrogen from biomass via pyrolysis: relationships between yield of hydrogen and temperature. *Energy Sources* 26:1061–1069.
- Dauvillee, D., Chochois, V., Steup, M., Haebel, S., Eckermann, N., Ritte, G., Ral, J.P., Colleoni, C., Hicks, G., Wattebled, F., Deschamps, P., D'hulst, C., Lienard, L., Cournac, L., Putaux, J.L., Dupeyre, D., Ball, S.G. 2006. Plastidial phosphorylase is required for normal starch synthesis in *Chlamydomonas reinhardtii*. *Plant J* 48:274–285.
- Feng, W., van der Kooi, H.J., Arons, J.D.S. 2004. Biomass conversions in subcritical and supercritical water: driving force, phase equilibria, and thermodynamic analysis. *Chem Eng Proc* 43:1459–1467.
- Friedrich, K., Kordesch, K., Simader, G., Selan, M. 1995. The process cycle sponge-iron/hydrogen/iron oxide used for fuel conditioning in fuel cells. *Proceedings of International Symposium on Fuel Cell System*, New York.
- Gadhe, J.B., Gupta, R.B. 2007. Hydrogen production by methanol reforming in supercritical water: catalysis by in situ-generated copper nanoparticles. *Int J Hydrogen Energy* 32:2374–2381.
- Gaffron, H. 1939. Reduction of carbon dioxide with molecular hydrogen in green algae. *Am J Bot* 27:273–283.
- Gaffron, H. 1940. Carbon dioxide reduction with molecular hydrogen in green algae. *Am J Bot* 27:273–283.
- Gaffron, H., Rubin, J. 1942. Fermentative and photochemical production of hydrogen in algae. *J Gen Physiol* 26:219–240.
- Gercel, H.F. 2002. The effect of a sweeping gas flow rate on the fast pyrolysis of biomass. *Energy Sources* 24:633–642.
- Gest, H., Kamen, M.D. 1949a. Studies on the metabolism of photosynthetic bacteria; photochemical production of molecular hydrogen by growing cultures of photosynthetic bacteria. *J Bacteriol* 58:239–245.
- Gest, H., Kamen, M.D. 1949b. Photoproduction of molecular hydrogen by *Rhodospirillum rubrum*. *Science* 109:558–559.
- Gest, H., Blankenship, R.E. 2004. Time line of discoveries: anoxygenic bacterial photosynthesis. *Photosynthesis Res* 80:59–70.
- Gfeller, R.P., Gibbs, M. 1984. Fermentative metabolism of *Chlamydomonas reinhardtii*: I. Analysis of fermentative products from starch in dark-light. *Plant Physiology* 75:212–218.

- Groenestijn, J.W.V., Hazewinkel, J.H.O., Nienoord, M., Bussmann, P.J.T. 2002. Energy aspects of biological hydrogen production in high rate bioreactors operated in the thermophilic temperature range. *Int J Hydrogen Energy* 27:1141–1147.
- Guan, Y.F., Deng, M.C., Yu, X.J., Zhang, W. 2004. Two-stage photobiological production of hydrogen by marine green alga *Platymonas subcordiformis*. *Biochem Eng J* 19:69–73.
- Guo, L.J., Lu, Y.J., Zhang, X.M., Ji, C.M., Guan, Y., Pei, A.X. 2007. Hydrogen production by biomass gasification in supercritical water: a systematic experimental and analytical study. *Catal Today* 129:275–286.
- Hallenbeck, P.C., Benemann, J.R. 2002. Biological hydrogen production; fundamentals and limiting processes. *Int J Hydrogen Energy* 27:1185–1193.
- Han, S.-K., Shin, H.-S. 2004. Biohydrogen production by anaerobic fermentation of food waste. *Int J Hydrogen Energy* 29:569–577.
- Hao, X.H., Guo, L.J., Mao, X., Zhang, X.M., Chen, X.J. 2003. Hydrogen production from glucose used as a model compound of biomass gasified in supercritical water. *Int J Hydrogen Energy* 28:55–64.
- Hao, X.H., Guo, L.J., Zhang, X.M., Guan, Y. 2005. Hydrogen production from catalytic gasification of cellulose in supercritical water. *Chem Eng J* 110:57–65.
- Hawkes, F.R., Dinsdale, R.M., Hawkes, D.L., Huss, I. 2002. Sustainable fermentative hydrogen production: challenges for process optimization. *Int J Hydrogen Energy* 27:1339–1347.
- Howarth, D.C., Codd, G.A. 1985. The uptake and production of molecular hydrogen by unicellular cyanobacteria. *J Gen Microbiol* 131:1561–1569.
- Hussy, I., Hawkes, F.R., Dinsdale, R., Hawkes, D.L. 2005. Continuous fermentative hydrogen production from sucrose and sugarbeet. *Int J Hydrogen Energy* 30:471–483.
- Kamen, M.D., Gest, H. 1949. Evidence for a nitrogenase system in the photosynthetic bacterium *Rhodospirillum rubrum*. *Science* 109:560.
- Klas, D. 2004. Biomass for renewable energy and fuels. *Encyclopedia of energy*. Elsevier, Oxford.
- Kruse, A., Meier, D., Rimbrecht, P., Schacht, M. 2000. Gasification of pyrocatechol in supercritical water in the presence of potassium hydroxide. *Ind Eng Chem Res* 39:4842–2848.
- Koskinen, P.E.P., Kaksonen, A.H., Puhakka, J.A. 2007. The relationship between instability of H_2 production and compositions of bacterial communities within a dark fermentation fluidized-bed bioreactor. *Biotechnol Bioeng* 97:742–758.
- Kotay, S.M., Das, D. 2008. Biohydrogen as a renewable energy resource: prospects and potentials. *Int J Hydrogen Energy* 33:258–263.
- Ledjeff-Hey, K., Kalk, T., Mahlendorf, F., Niemzig, O., Trautman, A., Roes, J. 2000. Portable PEFC generation with propane as fuel. *J Power Sources* 86:166–172.
- Levin, D.B., Pitt, L., Love, M. 2004. Biohydrogen production: prospects and limitations to practical application. *Int J Hydrogen Energy* 29:173–85.
- Li, S., Xu, S., Liu, S., Yang, C., Lu, Q. 2004. Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas. *Fuel Proc Technol* 85:1201–1211.
- Lindblad, P., Christensson, K., Lindberg, P., Fedorov, A., Pinto, F., Tsygankov, A. 2002. Photoproduction of H_2 by wildtype *Anabaena* PCC 7120 and a hydrogen uptake deficient mutant: from laboratory experiments to outdoor culture. *Int J Hydrogen Energy* 27:1271–1281.
- Lower, H.H. 1963. Chemistry of coal utilization, Suppl vol. Wiley, New York, pp. 740–815.
- Lu, Y., Guo, L., Zhang, X., Yan, Q. 2007. Thermodynamic modeling and analysis of biomass gasification for hydrogen production in supercritical water. *Chem Eng J* 131:233–244.
- Lu, Y.J., Jin, H., Guo, L.J., Zhang, X.M., Cao, C.Q., Guo, X. 2008. Hydrogen production by biomass gasification in supercritical water with a fluidized bed reactor. *Int J Hydrogen Energy* 33:6066–6075.
- Madamwar, D., Garg, N., Shah, V. 2000. Cyanobacterial hydrogen production. *World J Microbiol Biotechnol* 16:757–767.
- Maschio, G., Lucchesi, A., Stoppato, G. 1994. Production of syngas from biomass. *Biores Technol* 48:119–126.

- Masukawa, H., Mochimaru, M., Sakurai, H. 2002. Hydrogenases and photobiological hydrogen production utilizing nitrogenase system in cyanobacteria. *Int J Hydrogen Energy* 27:1471–1474.
- Melis, A., Happe, T. 2001. Hydrogen production. Green algae as a source of energy. *Plant Physiol* 127:740–48.
- Melis, A., Melnicki, M.R. 2006. Integrated biological hydrogen production. *Int J Hydrogen Energy* 31:1563–1573.
- Mertens, R., Liese, A. 2004. Biotechnological applications of hydrogenases. *Curr Opin Biotechnol* 15:343–348.
- Miao, X., Wu, Q. 2004. High yield bio-oil production from fast pyrolysis by metabolic controlling of *Chlorella protothecoides*. *J Biotechnol* 110:85–93.
- Midilli, A., Rzaev, P., Hayati, O., Teoman, A. 2000. Solar hydrogen production from hazelnut shells. *Int J Hydrogen Energy* 25:723–732.
- Milne, T.A., Elam, C.C., Evans, R.J. 2002. Hydrogen from biomass: state of the art and research challenges 1–82. National Renewable Energy Laboratory, Golden, CO.
- Minowa, T., Zhen, F., Ogi, T. 1997. Cellulose decomposition in hot-compressed water with alkali or nickel catalyst. *J. Supercritical Fluids* 13:253–259.
- Miura, Y. 1995. Hydrogen production by biophotolysis based on microalgal photosynthesis. *Proc Biochem* 30:1–7.
- Miura, Y., Akano, T., Fukatsu, K., Miyasaka, H., Mizoguchi, T., Yagi, K., Maeda, I., Ikuta, Y., Matsumoto, H. 1997. Stably sustained hydrogen production by biophotolysis in natural day/night cycle. *Energy Conver Manage* 38:S533–S537.
- Miura, Y., Akano, T., Fukatsu, K., Miyasaka, H., Mizoguchi, T., Yagi, K., Maeda, I., Ikuta, Y., Matsumoto, H. 1995. Hydrogen production by photosynthetic microorganisms. *Energy Convers Manage* 36:903–906.
- Mohan, D., Pittman, C.U., Steele, P.H. 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* 20:848–889.
- Nandi, R., Sengupta, S. 1998. Microbial production of hydrogen: an overview. *Critical Rev Microbiol* 24:61–84.
- Nath, K., Das, D. 2003. Hydrogen from biomass. *Current Sci* 85:265–271.
- Nath, K., Das, D. 2004. Biohydrogen production as a potential energy resource: present state-of-art. *J Sci Ind Res* 63:729–738.
- Ormerod, J.G., Gest, H. 1962. IV. Hydrogen photosynthesis and alternative metabolic pathways in photosynthetic bacteria. *Bacteriol Rev* 26:51–66.
- Ormerod, J.G., Ormerod, K.S., Gest, H. 1961. Light-dependent utilization of organic compounds and photoproduction of molecular hydrogen by photosynthetic bacteria; relationships with nitrogen metabolism. *Arch Biochem Biophys* 94:449–463.
- Patil, K.Z. 1987. Hydrogen. *Chem Age India* 38:519–527.
- Paul, P.F.M., Wise, W.S. 1971. The principle of gas extraction. Mills and Boon, London.
- Prince, R.C., Kheshgi, H.S. 2005. The photobiological production of hydrogen: potential efficiency and effectiveness as a renewable fuel. *Crit Rev Microbiol* 31:19–31.
- Putun, A.E. 2002. Biomass to bio-oil via fast pyrolysis of cotton straw and stalk. *Energy Sources* 24:275–285.
- Rapagna, F.P.U. 1996. Hydrogen from biomass by steam gasification. *Hydrogen Energy Progress XI, Proceedings of the 11th World Hydrogen Energy Conference, Stuttgart, Germany, 23–28 June 1996*, 1:907–912.
- Rapagna, S., Foscolo, P.U. 1998. Catalytic gasification of biomass to produce hydrogen-rich gas. *Int J Hydrogen Energy* 23:551–557.
- Safrany, D.R. 1971. A potential large scale plasma process: synthesis of inexpensive hydrogen by using a thermonuclear device to vaporize waste organic materials. *Chem Eng Progress Symp Ser* 67:103–108.
- Salmenoja, K. 1993. Black-liquor gasification: theoretical and experimental studies. *Biores Technol* 46:167–171.
- Sasikala, K., Ramana, C.V., Rao, P.R., Kovacs, K.L. 1993. Anoxygenic phototrophic bacteria: physiology and advances in hydrogen technology. *Adv Appl Microbio* 38:211–295.

- Serebryakova, L.T., Sheremetieva, M., Tsygankov, A. 1998. FEMS Microbiology Lett 166:89.
- Shahbazov, Sh.J., Usupov, I. 1994. Non-trading sources of energy for hydrogen. Int J Hydrogen Energy 19:863–864.
- Stevens, D.J. 2001. Hot gas conditioning: Recent progress with larger-scale biomass gasification systems. National Renewable Energy Laboratory, NREL/SR-510-29952, Golden, CO.
- Sung, S. 2004. Biohydrogen production from renewable organic wastes. Final Technical Report. Iowa State University, Ames, IA.
- Susta, M.R., Luby, P., Mat, S.B. 2003. Biomass energy utilization and environment protection commercial reality and outlook, Power Gen Asia. http://www.powergeneration.siemens.com/download/pool/industrialheatpower_02.pdf. Accessed 2009.
- Tran, D.Q., Charanjit, R. 1978. A kinetic model for pyrolysis of Douglas fir bark. Fuel 57:293–298.
- Tsygankov, A.A., Kosourov, S.N., Tolstygina, I.V., Ghirardi, M.L., Seibert, M. 2006. Hydrogen production by sulfur-deprived *Chlamydomonas reinhardtii* under photoautotrophic conditions. Int J Hydrogen Energy 31:1574–1585.
- Van Ginkel S., Sung, S., Lay, J.J. 2001. Biohydrogen production as a function of pH and substrate concentration. Environ Sci Technol 35:4726–4730.
- Van Ginkel, S.W., Logan, B. 2005. Increased biological hydrogen production with reduced organic loading. Water Res 39:3819–3826.
- Vayisoglu, E.S., Bartle, K.D., Erbatur, N.G., Frere, B., Snape, C.E., Erbatur, O. 1996. Chemical composition of SFE extracts obtained from coal and maceral concentrates. Fuel Process Technol 46:99–115.
- Vijayaraghavan, K., Soom, M.A.M. 2006. Trends in biohydrogen generation: a review. Environ Sci 3:255–271.
- Viswanathan, B. 2006. An introduction to energy sources. Indian Institute of Technology, Madras, India.
- Wagner, E.S., Froment, G.F. 1992. Steam reforming analyzed. Hydrocarbon Proc July:69–77.
- Walcher, G., Girges, S., Weingartner, S. 1996. Hydrogen Energy Progress XI, Proceedings of the 11th World Hydrogen Conference, 1996, Stuttgart.
- Wang, D., Czernik, S., Montane, D., Mann, M., Chornet, E. 1997. Biomass to hydrogen via fast pyrolysis and catalytic steam reforming of the pyrolysis oil or its fractions. Ind Eng Chem Res 36:1507–1518.
- Wang, D., Czernik, S., Chornet, E. 1998. Production of hydrogen from biomass by catalytic steam reforming of fast pyrolysis oils. Energy Fuels 12:19–24.
- Warnecke, R. 2000. Gasification of biomass: comparison of fixed bed and fluidized bed gasifier. Biomass Bioenergy 18:489–497.
- Watanabe, M., Iida, T., Inomata, H. 2006. Decomposition of a long chain saturated fatty acid with some additives in hot compressed water. Energy Convers Manage 47:3344–3350.
- Weissman, J.C., Benemann, J.R. 1977. Hydrogen production by nitrogen-starved cultures of *Anaerobaculum cylindrica*. Appl Environ Microbiol 33:123.
- White, A.L., Melis, A. 2006. Biochemistry of hydrogen metabolism in *Chlamydomonas reinhardtii* wild type and a Rubisco-less mutant. Int J Hydrogen Energy 31:455–465.
- Yan, Q., Guo, L., Lu, Y. 2006. Thermodynamic analysis of hydrogen production from biomass gasification in supercritical water. Energy Convers Manage 47:1515–1528.
- Yanik, J., Ebale, S., Kruse, A., Saglam, M., Yuksel, M. 2007. Biomass gasification in supercritical water: Part I. Effect of the nature of biomass. Fuel 86:2410–2415.
- Yogev, A., Kribus, A., Epstein, M., Kogan, A. 1998. Solar tower reflector systems: a new approach for high-temperature solar plants. Int J Hydrogen Energy 23:239–245.